

# Frequency Shifts in the Hyperfine Spectra of Alkalis Caused by Foreign Gases

LAWRENCE BAYLOR ROBINSON

*Space Technology Laboratories, Incorporated, Los Angeles, California*

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The pressure shift and the temperature coefficient of the pressure shift have been calculated for hyperfine spectra when radiating alkali atoms are perturbed by foreign gases. The method of calculation is based on a suggestion by H. Margenau. Both the pressure shift and the temperature coefficient can be calculated on the basis of potential functions representing intermolecular forces operative when the radiating atom is in the presence of the perturbing atoms. The noble gas atoms have been considered explicitly as perturbing atoms.

For weak interactions (small perturbing atoms) a Lennard-Jones (6-12) potential is adequate to give excellent agreement between theory and experiment. Helium and neon give rise to weak interactions and the frequency shifts are toward the blue. When the interactions are strong (large perturbing atoms), a simple Lennard-Jones (6-12) potential is no longer adequate to

give reasonable agreement between theory and experiment. When higher order attractive terms are included in the interaction, the agreement between theory and experiment is considerably improved. Argon and krypton give rise to strong interactions and frequency shifts toward the red.

Numerical values are obtained for the dipole-dipole, dipole-quadrupole, dipole-octupole, and quadrupole-quadrupole terms in the intermolecular interaction. For each pair of interacting atoms, there are two parameters to fit two sets of data. For the case of the small perturbing atoms, one of the parameters is just the sum of the gas kinetic radii, so that there is essentially only one parameter which is adjusted to fit two pieces of data.

The over-all agreement between theory and experiment is very good.

## I. INTRODUCTION

A FOREIGN (buffer) gas causes the central frequency of the spectral lines of a radiating atom to be displaced from its unperturbed position. This so-called pressure shift has been observed recently in hyperfine transitions in rubidium<sup>1</sup> and cesium.<sup>2</sup> Small atoms, of which helium and neon are examples, interacting with the alkali atoms shift the central frequency of the hyperfine line toward the blue (positive frequency shifts), whereas large atoms (e.g., argon and krypton) shift the central frequency toward the red (negative frequency shifts).

Margenau, Fontana, and Klein<sup>3</sup> have calculated the magnitudes of these pressure shifts on the basis of the well-known statistical theory for the effects of perturbing atoms on radiating atoms. Their expression for obtaining the frequency (or pressure) shift is

$$\bar{\nu} = \frac{4\pi N}{h} \int_0^\infty U(r) r^2 dr, \quad (1)$$

where  $r$  is the distance between perturbing atom and radiation atom,  $U(r)$  is the difference in energy levels (of the perturbed alkali atom) which give rise to the hyperfine line in question, and  $N$  is the particle density (number of atoms per unit volume) of perturbing gas atoms. Equation (1) is based on the assumption of a uniform distribution of perturbing gas atoms everywhere.

A method of improving the formulation of the interpretation of this pressure shift has been suggested to this writer by Margenau.<sup>4</sup> In this new formulation,

the distribution of perturbing atoms is not taken as uniform; in the vicinity of the radiating atom, the density of perturbing atoms is governed by the Boltzmann factor. Upon the introduction of this nonuniform density, based on the Boltzmann factor which contains the gas temperature, one can calculate the temperature coefficient of the pressure shift (as well as the pressure shift itself).

Instead of Eq. (1), the pressure shift  $\bar{\nu}$  in this present formulation is

$$\bar{\nu} = \frac{4\pi N}{h} \int_0^\infty \left\{ \exp \left[ -\frac{V(r)}{kT} \right] \right\} U(r) r^2 dr, \quad (2)$$

where  $V(r)$  is the potential between an alkali gas atom and a buffer gas atom. The temperature coefficient of the pressure shift is

$$\alpha = \frac{d\bar{\nu}}{dT} = \frac{4\pi N}{hkT^2} \int_0^\infty \left\{ \exp \left[ -\frac{V(r)}{kT} \right] \right\} U(r) V(r) r^2 dr. \quad (3)$$

In the next section, the methods of obtaining suitable forms for the potentials  $U(r)$  and  $V(r)$  will be discussed.

## II. THE INTERMOLECULAR POTENTIALS

It is well known that both  $U(r)$  and  $V(r)$  are negative (attractive) for large  $r$  and positive (repulsive) for small  $r$ . It is also well known that the long-range attractive part of such potentials varies as  $r^{-6}$ . At smaller intermolecular distances, higher order attractive terms become significant. When the intermolecular distance becomes very small (i.e., of the order of gas kinetic diameters) the interaction is characterized by repulsion rather than attraction. Very little is known about the precise form of the repulsive part of the potential.

<sup>1</sup> Bender, Beaty, and Chi, *Phys. Rev. Letters* **1**, 311 (1958).

<sup>2</sup> Beaty, Bender, and Chi, *Phys. Rev.* **112**, 450 (1958); M. Arditi and T. R. Carver, *Phys. Rev.* **112**, 449 (1958).

<sup>3</sup> Margenau, Fontana, and Klein, *Phys. Rev.* **115**, 87 (1959).

<sup>4</sup> Private communication from H. Margenau during his visit to Space Technology Laboratories, Inc., as consultant, June 22-24, 1959.

Two types of potentials have been used in the present calculations: (1) the Lennard-Jones (6-12) potential for  $V(r)$  and (2) the Lennard-Jones (6-12) potential with added  $r^{-8}$  and  $r^{-10}$  attractive terms for  $U(r)$ . These potentials are

$$V(r) = 4\epsilon_1[(\sigma_1/r)^{12} - (\sigma_1/r)^6], \quad (4)$$

and

$$U(r) = 4\epsilon_2[(\sigma_2/r)^{12} - (\sigma_2/r)^6] - (D_1/r^8) - (D_2/r^{10}). \quad (5)$$

One could add higher order attractive terms to the form of  $V(r)$ , but this would make no essential difference in the results in the present problem; furthermore, the mathematical aspects would become more complicated. The results of the calculation are more sensitive to  $U(r)$  and hence  $U(r)$  must be given more accurately. The basic difference between the forms of Eqs. (4) and (5) is the manner in which the repulsive parts of the potential are weighted. The standard Lennard-Jones

(6-12) potential, Eq. (4), essentially combines higher order attractive terms with repulsive terms to give a net  $r^{-12}$  repulsion. Equation (5) weights the repulsive part of the potential less heavily than Eq. (4) and also keeps the repulsive and higher order attractive terms separate.

There are several reasons for using such semiempirical potentials as given in Eqs. (4) and (5). In the first place, these potentials have the correct qualitative behavior and are adequate to describe interactions between many types of gas molecules. Secondly, such potentials are handled easily from the mathematical standpoint. Thirdly, the constants  $\epsilon_1\sigma_1^6$ ,  $\epsilon_2\sigma_2^6$ ,  $D_1$ , and  $D_2$  are easily calculated.

In Eqs. (4) and (5), the negative terms represent what is called the van der Waals energy. The van der Waals energy,<sup>5</sup>  $\Delta E_v$ , between a noble gas atom and an alkali atom is

$$\Delta E_v = - \sum_{L,l=1}^{\infty} \sum_M \left( \frac{\epsilon^4}{r^{2L+2l+2}} \frac{f_1 f_2 [(2L-1)!!(2L-1)!!(l+L)!(l+L)!]}{(2\beta_1)^L (2\beta_2)^L (l-M)!(l+M)!(L-M)!(L+M)! (\bar{E} + LI_2)} \right), \quad (6)$$

where the  $M$  is the smaller of  $L$  or  $l$  and takes on values from minus  $L$  (or  $l$ ) to plus  $L$  (or  $l$ ). In Eq. (6),  $L$  refers to the noble gas atom and  $l$ , to the alkali.  $(2L-1)!!$  means  $1 \cdot 3 \cdot 5 \cdots (2L-1)$ ,  $f_1$  is the mean oscillator strength for transitions between the  $P$  and  $S$  levels of the alkali and  $f_2$  is the mean oscillator strength for the noble gas atom; both oscillator strengths are taken as unity in these calculations.  $I_2$  is the ionization potential for the noble gas atom and  $\bar{E}$  is the weighted mean energy of the  $P$  states of the alkali (the energy of the  $S$  states is taken as zero). More specifically

$$\bar{E} = \frac{2}{3}F(P_{\frac{3}{2}}) + \frac{1}{3}E(P_{\frac{1}{2}}) - E(S_{\frac{1}{2}}).$$

Also,

$$1/\beta_1 = (\hbar)^2/m\bar{E}, \quad (7) \quad \text{and}$$

where  $m$  is the mass of the electron, and

$$1/\beta_2 = \alpha_2 I_2 / f_2 \epsilon^2, \quad (8)$$

where  $\alpha_2$  is the polarizability of the noble gas atom.

One may write Eq. (6) as

$$\Delta E_{\text{dis}} = -(C_{11}/r^6) - [(C_{12} + C_{21})/r^8] - \{[C_{22} + (C_{13} + C_{31})]/r^{10}\} - \cdots \quad (10)$$

The terms  $C_{Ll}/r^{(2L+2l+2)}$  represent dipole-dipole interactions when  $L=l=1$ ; dipole-quadrupole when  $L=1$ ,  $l=2$ , or  $L=2$ ,  $l=1$ ; quadrupole-quadrupole when  $L=l=2$ ; they are dipole-octupole when  $L=1$ ,  $l=3$ , or  $L=3$ ,  $l=1$ ; etc. Margenau, Fontana, and Klein have written the dipole-dipole terms explicitly and this writer has evaluated Eq. (6) for the cases of dipole-quadrupole, quadrupole-quadrupole and dipole-octupole terms. Numerical values for the coefficients are calculated in this article.

The difference in the van der Waals energy  $\Delta E_{\text{hyp}}$  between the levels which give rise to the hyperfine lines is given by<sup>3,5</sup>

$$\Delta E_{\text{hyp}} = \Delta E_v [\Delta\epsilon/(\bar{E} + I_2)], \quad (11)$$

where  $\Delta\epsilon$  is the actual energy separation of the unperturbed hyperfine levels.

From Eqs. (4), (5), and (10),

$$4\epsilon_1\sigma_1^6 = C_{11}, \quad (12)$$

$$4\epsilon_2\sigma_2^6 = C_{11}[\Delta\epsilon/(\bar{E} + I_2)] = a, \quad (13)$$

$$D_1 = (C_{12} + C_{21})[\Delta\epsilon/(\bar{E} + I_2)], \quad (14)$$

$$D_2 = [C_{22} + (C_{13} + C_{31})][\Delta\epsilon/(\bar{E} + I_2)]. \quad (15)$$

It follows from Eqs. (6) and (10) that

$$C_{11} = -\frac{3(\epsilon\hbar)^2 f_1}{2} \frac{\alpha_2 I_2}{m\bar{E}(\bar{E} + I_2)}, \quad (16)$$

$$(C_{12} + C_{21}) = \frac{45(\epsilon\hbar)^2 f_1 \alpha_2 I_2}{8} \frac{1}{m\bar{E} \epsilon^2} \times \left( \frac{(\epsilon\hbar)^2}{m\bar{E}(2\bar{E} + I_2)} + \frac{\alpha_2 I_2}{f_2(\bar{E} + 2I_2)} \right), \quad (17)$$

$$C_{22} = \frac{315 f_1}{16} \frac{(\epsilon\hbar)^4}{f_2 (m\bar{E})^2} \frac{\alpha_2^2 I_2^2}{(\bar{E} + I_2)\epsilon^4}, \quad (18)$$

<sup>5</sup> Private communication from P. Fontana of Yale University.

TABLE I. Parameters involved in the interaction between buffer gas and alkali atoms.

Buffer gas	$a$ in units of $10^{-66}$ erg cm <sup>6</sup>		$C_{11}$ in units of $10^{-60}$ erg cm <sup>6</sup>		$D_1$ in units of $10^{-80}$ erg cm <sup>8</sup>		$D_2$ in units of $10^{-95}$ erg cm <sup>10</sup>	
	Rb	Cs	Rb	Cs	Rb	Cs	Rb	Cs
He	34.9	52.5	30.9	34.3	6.25	10.3	22.1	40.6
Ne	63.6	95.5	59.4	65.5	13.5	22.5	47.8	86.2
A	371	558	242	269	77.0	135	276	533
Kr	645	975	349	394	139	237	508	916
N <sub>2</sub>	430	650	264	295	89.3	147	321	582

and

$$(C_{13} + C_{31}) = \frac{1565 f_1 (\epsilon \hbar)^2}{36 \epsilon^4 m \bar{E}} \alpha_2 I_2 \times \left( \frac{(\epsilon \hbar)^4}{(m \bar{E})^2} \frac{1}{(3 \bar{E} + I_2)} + \frac{(\alpha_2 I_2)^2}{f_2 (\bar{E} + 3 I_2)} \right). \quad (19)$$

The above expressions differ from those based on the usual London formula<sup>6</sup> in that  $(\epsilon \hbar)^2/m \bar{E}$  is used above in place of  $\alpha_1 I_1$  (for the alkali) in the London formula. The level spacings in the alkali atoms makes it so that Eqs. (16), (17), (18), and (19) are more accurate than the London formulas.

The calculated values of the parameters to be used in determining the pressure and temperature shifts are given in Table I. The van der Waals coefficient,  $C_{11}$ , is repeated in Table II in order to show how the values used in this article compare with other listings.

### III. THE PRESSURE SHIFT

In order to evaluate the integral for the pressure shift of the hyperfine frequencies, given in Eq. (2), it is convenient to make the following substitutions:

$$t = (\sigma_1/r)^6, \quad (20)$$

$$\gamma = (\sigma_2/\sigma_1)^6, \quad (21)$$

$$\beta^2 = \epsilon_1/kT. \quad (22)$$

TABLE II. The dispersion constant in the van der Waals interaction.

Buffer gas	Alkali	$C_{11}$ in units of $10^{-60}$ erg cm <sup>6</sup>					
		b	c	d	b	c	d
He		25.4	40	30.9	29.4	44	34.3
Ne		49.0	77	59.4	56.7	87	65.5
A		249	290	242	235	325	269
Kr				349			394
N <sub>2</sub>				264			295

<sup>a</sup> The numbers in the column marked b and c are taken from H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, New York, 1952), p. 397. A measured value of 370 is also listed for the He-Cs interaction.

<sup>b</sup> Measured by collision cross section technique.

<sup>c</sup> Calculated by H. S. W. Massey and E. H. S. Burhop.

<sup>d</sup> Calculated in this article.

<sup>6</sup> E.g., Hirshfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 965.

It follows that

$$V(r)/kT = 4\beta^2(\ell^2 - t), \quad (23)$$

and

$$U(r) = 4\epsilon_2(\gamma^2 \ell^2 - \gamma t) - (D_1/\sigma_1^8) t^{4/3} - (D_2/\sigma_2^{10}) t^{5/3}. \quad (24)$$

Equation (2) becomes

$$\begin{aligned} \bar{\nu} = & \frac{8\pi N}{3} \frac{1}{h} \epsilon_2 \gamma \sigma_1^3 \left\{ \gamma \int_0^\infty t^{1/2} \exp[-4\beta^2(\ell^2 - t)] dt \right. \\ & \left. - \int_0^\infty t^{-1/2} \exp[-4\beta^2(\ell^2 - t)] dt \right\} \\ & - \frac{2\pi N D_1}{3} \frac{1}{h \sigma_1^5} \left\{ \int_0^\infty t^{-1/6} \exp[-4\beta^2(\ell^2 - t)] dt \right. \\ & \left. + \frac{D_1}{\sigma_1^2 D_1} \int_0^\infty t^{1/6} \exp[-4\beta^2(\ell^2 - t)] dt \right\}. \quad (25) \end{aligned}$$

It will be convenient to use the following substitution:

$$I(x, \beta) = \int_0^\infty t^x \exp[-4\beta^2(\ell^2 - t)] dt. \quad (26)$$

Equation (25) can be written more compactly as

$$\begin{aligned} \bar{\nu} = & (8\pi/3)(N/h) \epsilon_2 \gamma \sigma_1^3 [\gamma I(\frac{1}{2}, \beta) - I(-\frac{1}{2}, \beta)] \\ & - (2\pi/3)(N/h) (D_1/\sigma_1^5) \\ & \times [I(-\frac{1}{6}, \beta) + (D_2/\sigma_1^2 D_1) I(\frac{1}{6}, \beta)]. \quad (27) \end{aligned}$$

Equation (27) can be written in terms of the two parameters,  $\beta$ , and  $\gamma$ . If one divides Eq. (13) by Eq. (12), he obtains

$$\epsilon_2 = (a/C_{11})(\epsilon_1/\gamma), \quad (28)$$

and from Eq. (22), the above may be written

$$\epsilon_2 = (a/C_{11})(kT\beta^2/\gamma). \quad (29)$$

From Eqs. (12) and (22)

$$\sigma_1 = C_{11}^{1/6}/(4kT)^{1/6} \beta^{1/3}. \quad (30)$$

Hence, Eq. (27) becomes

$$\begin{aligned} \bar{\nu}(\beta, \gamma) = & \frac{4\pi N}{3} \frac{a}{h C_{11}^{1/3}} (kT)^{1/3} \beta \\ & \times [\gamma I(\frac{1}{2}, \beta) - I(-\frac{1}{2}, \beta)] - \frac{2 N (4kT)^{5/6}}{3 h a^{5/6}} D_1 \beta^{5/3} \\ & \times \left[ I(-\frac{1}{6}, \beta) + \frac{D_2 (4kT)^{1/3}}{D_1 C_{11}^{1/3}} I(\frac{1}{6}, \beta) \right]. \quad (31) \end{aligned}$$

It is evident that  $\bar{\nu}(\beta, \gamma)$  can be positive or negative depending on the values of the various parameters.

#### IV. TEMPERATURE COEFFICIENT OF THE PRESSURE SHIFT

The same changes of variables, as used in connection with the pressure shift, will now be used in obtaining the temperature coefficient of the pressure shift [Eq. (3)]. One sees that

$$U(r)V(r) = 16\epsilon_1\epsilon_2\gamma[\gamma t^4 - (\gamma+1)t^3 + t^2] + 4\epsilon_1[(D_1/\sigma_1^8)(t^{7/3} - t^{10/3}) + (D_2/\sigma_1^{10})(t^{8/3} - t^{11/3})], \quad (32)$$

so that Eq. (3) becomes

$$\begin{aligned} \alpha = & (32\pi N/3hkT^2)\epsilon_1\epsilon_2\sigma_1^3\gamma \\ & \times [\gamma I(\frac{5}{2}, \beta) - (\gamma+1)I(\frac{3}{2}, \beta) + I(\frac{1}{2}, \beta)] \\ & + (8\pi N/3hkT^2)(\epsilon_1 D_1/\sigma_1^5)[I(5/6, \beta) - I(11/6, \beta)] \\ & + (8\pi N/3hkT^2)(\epsilon_1 D_2/\sigma_1^7) \\ & \times [I(7/6, \beta) - I(13/6, \beta)]. \quad (33) \end{aligned}$$

Because of Eqs. (29) and (30), one may write Eq. (33) as a function of the two parameters  $\beta$  and  $\gamma$ , so that

$$\begin{aligned} \alpha(\beta, \gamma) = & (4\pi/3)(N/hT)(a/C_{11}^{1/3})(kT)^{1/3}(4\beta^3) \\ & \times [\gamma I(\frac{5}{2}, \beta) - (\gamma+1)I(\frac{3}{2}, \beta) + I(\frac{1}{2}, \beta)] \\ & + (8\pi/3)(N/hT)(D_1/C_{11}^{5/6})(4kT)^{5/6} \\ & \times \beta^{11/3}[I(5/6, \beta) - I(11/6, \beta)] \\ & + (8\pi/3)(N/hT)(D_2/C_{11}^{7/6})(4kT)^{7/6} \\ & \times \beta^{13/3}[I(7/6, \beta) - I(13/6, \beta)]. \quad (34) \end{aligned}$$

As in the case of  $\bar{\nu}(\beta, \gamma)$ ,  $\alpha(\beta, \gamma)$  can be positive or negative depending on  $\beta$  and  $\gamma$ . It is also true that  $\alpha\bar{\nu} > 0$  or  $\alpha\bar{\nu} < 0$  depending on the parameters. The alkali atoms perturbed by noble gas atoms show  $\alpha$  and  $\bar{\nu}$  of the same sign. When the alkali atoms are perturbed by some hydrocarbons, then  $\alpha$  and  $\bar{\nu}$  have been found (experimentally) to be of opposite sign. For  $\beta > 0.6$ ,  $\alpha$  is positive, irrespective of the value of  $\gamma$ ; whereas  $\bar{\nu}$  can be positive or negative depending on the value of  $\gamma$ .

#### V. RESULTS

##### 1. Evaluation of Integrals

The first step involved in obtaining  $\bar{\nu}(\beta, \gamma)$  and  $\alpha(\beta, \gamma)$  is the evaluation of the integrals  $I(x, \beta)$  given in Eq. (26). Such integrals have been given in terms of confluent hypergeometric functions (also in terms of so-called Whittaker functions) in an extensive table of Mellin transforms.<sup>7</sup> Since the functions have not been tabulated (numerically) for the cases of interest, the Mellin transform table is of little use in the present problem.

There are various methods whereby one can evaluate the integrals, numerically. Two methods are given be-

low: the first method is useful for small  $\beta$  and the second method for large  $\beta$ .

In the first method, one makes the change of variable  $4\beta^2 t^2 = u$ , so that Eq. (26) becomes

$$\begin{aligned} I(x, \beta) = & \int_0^\infty t^x \exp[-4\beta^2(t^2 - t)] dt \\ = & \frac{1}{2(2\beta)^{x+1}} \int_0^\infty e^{-u} \exp(2\beta u^{1/2}) u^{(x-1)/2} du. \quad (35) \end{aligned}$$

When one writes

$$\exp(2\beta u^{1/2}) = \sum_{n=0}^{\infty} \frac{(2\beta)^n}{n!} u^{n/2},$$

it follows that

$$\begin{aligned} I(x, \beta) = & \frac{1}{(2\beta)^{x+1}} \sum_{n=0}^{\infty} \frac{(2\beta)^n}{2n!} \int_0^\infty e^{-u} u^{(n+x+1)/2} du \\ = & \frac{1}{(2\beta)^{x+1}} \sum_{n=0}^{\infty} \frac{(2\beta)^n}{2n!} \Gamma\left(\frac{n+x+1}{2}\right), \quad (36) \end{aligned}$$

where  $\Gamma[(n+x+1)/2]$  is the well-known gamma function.

It is evident that when  $\beta \ll 1$ , only a few terms in the sum given in Eq. (36) are significant. Hence, for very small values of  $\beta$ , the integrals  $I(x, \beta)$  are easily evaluated.

The second method involves writing the integral in Eq. (26) as

$$I(x, \beta) = \frac{\exp(\beta^2)}{(2\beta)^{x+1}} \int_0^\infty \exp[-(\xi - \beta)^2] \xi^x d\xi, \quad (37)$$

where  $4\beta^2 t^2 = \xi^2$ . The additional change of variable,  $(\xi - \beta) = \zeta$  converts Eq. (37) into

$$I(x, \beta) = \frac{\exp(\beta^2)}{(2\beta)^{x+1}} \int_{-\beta}^\infty \exp(-\zeta^2) (\zeta + \beta)^x d\zeta. \quad (38)$$

When  $\beta \gg 1$ , only a few terms are required in the expansion,

$$\begin{aligned} (\zeta + \beta)^x = & \beta^x [1 + (x\zeta/\beta) \\ & + [x(x-1)/2](\zeta^2/\beta^2) + \dots]. \quad (39) \end{aligned}$$

and one can replace the lower limit in the integral in Eq. (38) by  $-\infty$  without any significant error. Hence, Eq. (38) may be written as

$$\begin{aligned} I(x, \beta) = & \frac{\exp(\beta^2)}{(2\beta)^{x+1}} \beta^x \left[ \int_{-\infty}^\infty \exp(-\zeta^2) d\zeta \right. \\ & + \frac{x}{\beta} \int_{-\infty}^\infty \exp(-\zeta^2) \zeta d\zeta \\ & \left. + \frac{x(x-1)}{\beta^2} \int_{-\infty}^\infty \exp(-\zeta^2) \zeta^2 d\zeta + \dots \right]. \quad (40) \end{aligned}$$

<sup>7</sup> Erdelyi, Magnus, Oberhettinger, and Tricomi, *Table of Integral Transforms* (McGraw-Hill Book Company, Inc., New York, 1954), Vol. 1, p. 313, Table 6.3, entry 13; also p. 386.

TABLE III. Numerical values of  $I(x, \beta)$ .

$x \backslash \beta$	5/2	13/6	11/6	3/2	7/6	5/6	1/2	1/6	-1/6	-1/2
0.100	165.13	92.42	52.95	31.171	18.952	11.987	7.976	5.687	4.506	4.280
0.200	18.945	13.175	9.372	6.843	5.154	4.032	3.312	2.907	2.823	3.250
0.300	6.009	4.718	3.785	3.114	2.640	2.320	2.137	2.097	2.266	2.877
0.400	2.908	2.478	2.157	1.922	1.763	1.674	1.662	1.752	2.025	2.725
0.500	1.784	1.615	1.491	1.410	1.369	1.374	1.438	1.595	1.928	2.692
0.600	1.276	1.211	1.171	1.157	1.174	1.229	1.339	1.539	1.921	2.742
0.700	1.019	1.004	1.007	1.032	1.083	1.172	1.315	1.553	1.981	2.864
0.800	0.8856	0.8997	0.9300	0.9805	1.058	1.174	1.350	1.627	2.105	3.016
0.900	0.8234	0.8580	0.9091	0.9815	1.083	1.227	1.437	1.758	2.296	3.341
1.000	0.8096	0.8622	0.9326	1.027	1.154	1.330	1.580	1.955	2.568	3.724

The second integral vanishes as do all others involving odd powers of  $\xi$ ; the first integral and all others involving even powers of  $\xi$  are gamma functions.  $I(x, \beta)$ , for  $\beta \gg 1$ , is given by

$$I(x, \beta) = \frac{\exp(\beta^2)}{(2\beta)^{x+1}} (\pi)^{1/2} \left[ 1 + \frac{x(x-1)}{2\beta^2} + O(\beta^{-4}) \right], \quad (41)$$

where  $O(\beta^{-4})$  means the other terms are of the order of  $\beta^{-4}$  and smaller.

To cover the desired range of  $x$  and  $\beta$  adequately, the integrals  $I(x, \beta)$  were evaluated (for the values of  $x$  and  $\beta$  of interest) with the Space Technology Laboratories IBM-704 Electronic Computer. The results are given in Table III.

## 2. Comparison of Theory and Experiment

It seems clear that the experimental results can be interpreted on the basis of a variety of types of intermolecular potentials. The essential result of this article is the interpretation of the mechanism giving rise to pressure and temperature shifts, on the basis of well-known intermolecular potentials. For many values of  $\beta$ , there are corresponding values of  $\gamma$  which will reproduce the experimental values of  $\bar{\nu}$ . Also,  $\alpha$  can be calculated with several values of  $\beta$  and corresponding values of  $\gamma$ . However, there is just *one* value of  $\beta$  and *one* value of  $\gamma$  which will give the experimental values of both  $\bar{\nu}$  and  $\alpha$  for a given pair of atoms.

At this point, it is worthwhile observing that the temperature coefficient of the pressure shift is of the order of  $\bar{\nu}/T$ , for  $T=300^\circ\text{K}$ . For the case of positive (blue) shifts,  $\bar{\nu}=2T\alpha$ , approximately. One can see how this comes about by examining Eqs. (31) and (34). From Table III, it is evident that all  $I(x, \beta)$  are of the same order for  $0.4 < \beta < 0.3$ . Hence if  $\gamma \gg 1$ , then only the first term in Eq. (31) is significant. The terms  $\gamma I(\frac{5}{2}, \beta)$  tends to cancel  $-(\gamma+1)I(\frac{3}{2}, \beta)$  and only  $I(\frac{1}{2}, \beta)$  remains in Eq. (34). The higher order terms are neglected.

$$\bar{\nu} = \alpha T / 4\beta^2, \text{ approximately.} \quad (42)$$

When  $\beta=0.35$ , then  $\bar{\nu}=2\alpha T$ , in accordance with experi-

ment for frequency shifts toward the blue. When  $\gamma \ll 1$ , then negative (red) shifts result and the relationship between  $\bar{\nu}$  and  $\alpha$  is not so simple. Finally when  $\beta > 0.6$ , then  $\bar{\nu} < 0$  and  $\alpha > 0$ , practically independent of the value of  $\gamma$  (as long as  $\gamma$  is small enough to make  $\bar{\nu} < 0$ ). This latter situations obtains for interactions between the alkalis and some hydrocarbons.

TABLE IV. Calculated and experimental values of pressure and temperature shifts.<sup>a</sup>

Part 1. Results for small noble gas atoms				
	Rb-He	Rb-Ne	Cs-He	Cs-Ne
$\sigma_1(\text{\AA})$	3.24	3.43	3.39	3.58
$\epsilon_1(\text{ev})$	$4.16 \times 10^{-3}$	$5.36 \times 10^{-3}$	$3.52 \times 10^{-3}$	$4.85 \times 10^{-3}$
$\beta$	0.408	0.463	0.376	0.441
$\gamma$	42.0	18.5	50.0	18.0
$\sigma_2(\text{\AA})$	6.03	5.43	6.50	5.79
$\epsilon_2(\text{ev})$	$1.20 \times 10^{-9}$	$3.94 \times 10^{-9}$	$1.18 \times 10^{-9}$	$2.34 \times 10^{-9}$
$\bar{\nu}$ expt <sup>b,c</sup>	$+7200 \pm 140$	$+3920 \pm 80$	$+10\,500$	$+5800$
$\bar{\nu}$ expt <sup>b,d</sup>			$+16\,000$	$+6500$
$\bar{\nu}$ calc <sup>b</sup>	$+7200$	$+3820$	$+12\,000$	$+6100$
$\alpha$ expt <sup>e,o</sup>	$+10$	$+2.6$	$+15$	$+1$
$\alpha$ calc <sup>e</sup>	$+9.9$	$+4.2$	$+17$	$+3$
Part 2. Results for large noble gas atoms				
$\gamma \ll 1$	Rb-A	Rb-Kr	Cs-A	Cs-Kr
$\beta$	0.30	0.40	0.30	0.45
$\bar{\nu}$ expt <sup>b,c</sup>	$-510 \pm 10$	$-5800 \pm 500$	$-1900$	$-13\,000$
$\bar{\nu}$ expt <sup>b,d</sup>			$-2500$	$-13\,000$
$\bar{\nu}$ calc <sup>b</sup>	$-2100$	$-4100$	$-3300$	$-6640$
$\alpha$ expt <sup>e,o</sup>	$-3.0$	$-5$	$-7$	
$\alpha$ calc <sup>e</sup>	$-1.4$	$-2$	$-3$	$-3$
Part 3. Results for nitrogen molecules				
	Rb-N <sub>2</sub>		Cs-N <sub>2</sub>	
$\beta$	0.30		0.40	
$\gamma$	7.5		8.5	
$\bar{\nu}$ expt <sup>b,c</sup>	$+5200 \pm 100$		$+8900$	
$\bar{\nu}$ expt <sup>b,d</sup>			$+9300$	
$\bar{\nu}$ calc <sup>b</sup>	$+5300$		$+9000$	
$\alpha$ expt <sup>e,o</sup>	$+6$			
$\alpha$ calc <sup>e</sup>	$+4.4$		$+11$	

<sup>a</sup> Atomic radii (angstroms):  $R_{\text{He}}=0.93$ ,  $R_{\text{Ne}}=1.12$ ,  $R_{\text{Rb}}=2.31$ ,  $R_{\text{Cs}}=2.43$ . The atomic radii are taken from W. E. Forsythe, *Smithsonian Physical Tables* (Smithsonian Institution, Washington, D. C., 1951), ninth revised edition, p. 643. The values for Rb and Cs are the mean of the two values listed for each alkali.

<sup>b</sup> Cycles/sec/cm of mercury.

<sup>c</sup> See Beaty *et al.*, reference 2.

<sup>d</sup> See Arditi and Carver, reference 2.

<sup>e</sup> Cycles/sec/cm of mercury/deg C.

In comparing theory with experiment, the parameters  $\beta$  and  $\gamma$  must be found by trial and error. Unfortunately, theory has not developed to the point where these parameters can be calculated from first principles. From the point of view of the present formulation, the experiments on the frequency shifts *measure*  $\beta$  and  $\gamma$  and provide a very sensitive means of studying intermolecular forces.

It turned out rather unexpectedly that the Lennard-Jones (6-12) potential for both  $V(r)$  and  $U(r)$  will reproduce both  $\bar{\nu}$  and  $\alpha$  (almost to the same order of accuracy as the experiments) for Rb-He, Rb-Ne, Cs-He, and Cs-Ne interactions if one uses the sum of the gas kinetic radii of the interacting atoms for  $\sigma_1$  in Eq. (4). Since  $\sigma_1$  determines  $\beta$  through Eqs. (12) and (22), there is just one adjustable parameter,  $\gamma$ , to determine both  $\bar{\nu}$  and  $\alpha$ . In the strict Lennard-Jones (6-12) potential, the higher order attractive terms are combined with the repulsive terms to give a net  $r^{-12}$  attraction; hence  $D_1$  and  $D_2$  in Eq. (5) vanish for such a potential. The results of the present calculations for the interactions involving the small buffer gas atoms are shown in Table IV, Part 1. The agreement between theory and experiment is excellent.

For the cases of the larger buffer atoms, one cannot obtain reasonable agreement between theory and experiment without the higher order attractive terms. The

comparison between theory and experiment is given in Table IV, Part 2. The agreement between theory and experiment is very good, though not as close as in the case of positive frequency shifts. For the negative shifts,  $\gamma \ll 1$ . It might be helpful to note that small  $\gamma$  means steep repulsive forces, which one would indeed expect for the heavier rare gas atoms. This is in agreement with reference 3, where it was found that  $\bar{\nu}$  could be computed with a rigid exchange-force model.

Table IV, Part 3, contains the pressure and temperature shifts with molecular nitrogen. Here the parameters  $\gamma$  and  $\beta$  are selected to fit the data. As in the other cases of positive frequency shifts, the agreement between theory and experiment is excellent.

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