

Hyperfine pressure shift of ^{133}Cs atoms in noble and molecular buffer gases*

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The fractional pressure shifts (fps) of the ground-state hyperfine frequency of ^{133}Cs were remeasured for a number of buffer gases and found to be (in units of $10^{-9}/\text{Torr}$): for He, 123.5 ± 1.0 ; H_2 , 118.0 ± 0.5 ; Ne, 63.5 ± 0.5 ; N_2 , 90.0 ± 1.0 ; Ar, -21.5 ± 1.0 ; CH_4 , -104.0 ± 0.5 ; CD_3H , -92.5 ± 0.5 ; C_2H_6 , -188.5 ± 2.5 ; C_3H_8 , -291.5 ± 1.5 ; C_4H_{10} , -390.5 ± 2.5 ; and C_2H_4 , -269.0 ± 2.5 . In addition, the fps for the buffers D_2 , 188.0 ± 0.5 ; CF_4 , -21.5 ± 1.0 ; and CD_2H_2 , -95.5 ± 0.5 were measured for the first time. Trends in the observed fractional shifts are discussed qualitatively in terms of the effects of anisotropic intermolecular interactions on the long- and short-range contributions to the fps.

I. INTRODUCTION

Optical-pumping techniques^{1,2} provide a sensitive method by which small energy splittings in the ground and excited states of atoms and ions³ may be precisely determined. Measurements of the ground-state hyperfine intervals of paramagnetic atoms and ions by these methods are often performed in the presence of a buffer gas which is used to collisionally narrow the Doppler-broadened hyperfine lines⁴ as well as to decrease wall relaxation of the pumped species.⁵ Small shifts are observed in the hyperfine frequencies which arise from collisions of the atom or ion with the buffer⁶⁻¹³ and which may be either positive (blue) or negative (red), depending upon the buffer gas used. The shift contains information regarding the manner in which the interacting atoms are perturbed and thus complements other properties which depend on the intermolecular potential.¹⁴ Considerable effort has been expended toward providing a quantitative theoretical description of these shifts.^{14, 15}

The fractional pressure shift (fps) $(1/\nu_0)(\partial\nu/\partial p)_T$ of cesium in various buffer gases has been measured previously by a number of workers. Arditi and Carver^{11(a), 11(b)} and Beatty, Bender, and Chi^{11(c)} have measured the fps of cesium in the inert gas buffers He, Ne, Ar, Kr, and Xe as well as the molecular buffers H_2 and N_2 by optically detecting the field-independent $\Delta F = 1$ ($m_F = 0 \rightarrow m_F = 0$) hyperfine transition. Bernheim and Kohuth monitored the field-dependent $\Delta F = 1$, $\Delta m_F = -1$ hyperfine transition to measure the fps of cesium in a number of hydrocarbon buffers and observed an interesting trend in the fps with the polarizability of the buffer. However, the field-dependent transition which they observed was severely broadened by field inhomogeneities, and this detracted from the precision of the measurements.

The values of the fps of the cesium hyperfine frequency determined previously by other workers

are listed in the left-hand column of Table I. Some discrepancies between the values of the fps observed for the lighter rare gases, He, Ne, and Ar, as well as N_2 , are apparent. Also, the fps of cesium in H_2 is larger than that observed in He, a result which is at odds with the trend observed in the alkali metals ^{23}Na , ^{39}K , and ^{87}Rb , in which the fps of He is always larger than that of H_2 .

In the present work, we have remeasured the fps of cesium in a number of buffer gases with the intention of improving the data for the hydrocarbon buffer gases and resolving the discrepancies for He, Ne, Ar, N_2 , and H_2 . In addition, we present data for D_2 , CF_4 , and CH_2D_2 for the first time.

II. EXPERIMENTAL

In the present work, the field-dependent $\Delta F = 1$, $m_F = 4 \rightarrow 3$ hyperfine transition was measured instead of the field-independent $m_F = 0 \rightarrow m_F = 0$ transition. While the field-dependent transition in cesium is subject to drift in the applied field and broadening due to ac stray fields and magnetic field inhomogeneities, it is more convenient to observe than the 0-0 transition. The $F = 4$, $m_F = 4$ state is readily pumped by irradiating the sample with circularly polarized light in a weak magnetic field. In order to observe the 0-0 transition in cesium, one must make use of more complicated hyperfine pumping techniques.¹⁶

A diagram of the experimental apparatus is shown in Fig. 1. The microwave power was obtained from a Varian VA-153C x-band klystron which was phase-locked to a stable 4.990 58-MHz crystal oscillator by means of a Dymec 2654 A frequency synchronizer. A 29-31-MHz i.f. reference frequency, obtained from a Hewlett-Packard 606A signal generator, was injected into the Dymec synchronizer, allowing the klystron frequency to be varied over a 2-MHz range. The i.f. was swept at the rate of 47 Hz/sec using a clock motor. Short-term stability of the klystron output

TABLE I. Fractional pressure shifts with standard errors of the cesium hyperfine frequency for different buffer gases, determined in this work and by previous authors. Also included are the C_6 constants (see Ref. 23) which characterize the cesium-buffer dispersion forces.

	fps		C_6 (au)
	Previous work	This work	
He	174 ^a	123.5±1.0	45
	131 ^b		
	114 ^c		
Ne	71 ^a	63.5±0.5	87
	63 ^c		
Ar	-27 ^a	-21.5±1.0	350
	-23 ^b		
	-21 ^c		
Kr	-148 ^b	...	520
	-142 ^{a,c}		
Xe	-261 ^a	...	830
	-256 ^b		
H ₂	207 ^a	118.0±0.5	170
D ₂	...	118.0±0.5	168
N ₂	101 ^a	90.0±1.0	370
	97 ^c		
	90 ^b		
CH ₄	-116 ^d	-104.0±0.5	580
CD ₃ H	-96 ^d	-92.5±0.5	...
CD ₂ H ₂	...	-95.5±0.5	...
CF ₄	...	-21.5±1.0	663
C ₂ H ₆	-188 ^d	-188.5±2.5	997
C ₃ H ₈	-282 ^d	-291.5±1.5	1416
C ₄ H ₁₀	-370 ^d	-390.5±2.5	1819
C ₂ H ₄	-305 ^d	-269.0±2.5	928
C ₃ H ₆	-671 ^d	...	1369

^a Reference 11 (a).

^b Reference 11 (b).

^c Reference 11 (c).

^d Reference 11 (d).

was 2.3 Hz/sec. The klystron output was attenuated by 45–50 dB and amplitude modulated at 40 Hz by a Gyruline modulator before passing into a TE₀₁₁ mode cavity containing the vapor cell. Two square windows covered with screen allowed the pumping light to be transmitted through the cavity. The applied magnetic field was measured by observing the $m_F = 4 \rightarrow m_F = 3$ Zeeman transition. This transition was driven by a General Radio 805C oscillator, the output of which was amplitude modulated at 40 Hz and applied to several turns of No. 32 wire wrapped around the vapor cell. The oscillator was swept at the rate of 8–10 Hz/sec with a reversible electric motor. The klystron output frequency was measured using a Hewlett-Packard 2590A microwave frequency converter and an electric counter whose time base was compared to radio station WWVB using a Hewlett-Packard VLF comparator. This arrangement permitted an absolute accuracy of a few parts in 10^{10} to be obtained in the frequency

measurements. A second counter was used to measure the Zeeman frequency.

The light source used in this study was similar to the electrodeless design described by Franz.¹⁷ The D₂ component of the cesium resonance radiation was removed by an interference filter, and circularly polarized with Polaroid HN7 and a quarter-wave sheet. The intensity of the radiation passing through the vapor cell was measured with a silicon solar cell, the output of which was amplified, fed into a Princeton Applied Research JB-4 phase-sensitive amplifier, and displayed on a chart recorder.

The applied magnetic field used in this study was provided by three mutually perpendicular sets of Helmholtz coils. Two sets of coils were used to cancel the earth's magnetic field perpendicular to the direction of the pumping light while the third set was used to provide a 0.13-G field in the direction of the pumping beam. The effects of stray ac fields were minimized by placing the vapor cell cavity and detector inside an aluminum pipe 1 in. thick, 30 in. long, and 10 in. outside diameter. The pipe was oriented with its axis perpendicular to the pumping beam. A 1¼-in. hole drilled through the middle of the pipe admitted the pumping light. As a further measure to reduce the stray fields, the unused windings (about 180 turns) on the Helmholtz coils which produced the field parallel to the pumping light were shorted together.¹⁸ The effects of magnetic field gradients, arising from the distortion of the earth's field by the structural steel of the building and nearby apparatus, were minimized with magnetic-field-gradient windings on each pair of the Helmholtz coil forms. A magnetometer was used to map the field in the region about the vapor cell, and the current passing through the field-gradient coils was adjusted to minimize the gradients. One of the field gradients was too large to be minimized in this way and a method employing bar magnets was used to partial-

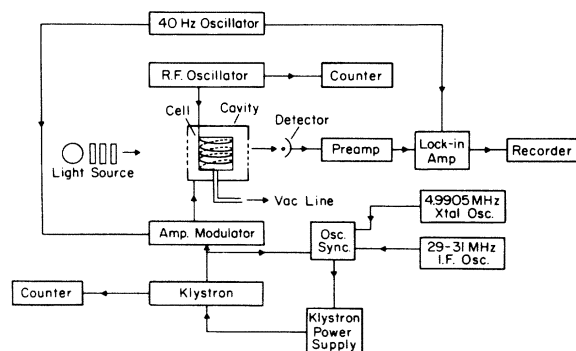


FIG. 1. Block diagram of the apparatus used to measure cesium hyperfine pressure shifts.

ly cancel it.¹⁹ The stray-field attenuation and field-gradient reduction decreased the Zeeman linewidth from 1 kHz to 100 Hz.

Rather than work with individual sample bulbs containing cesium and a known amount of buffer gas, a vapor cell directly connected to a gas filling system was used. Such an arrangement avoids the inconvenience resulting from the inaccessibility of the vapor cell and cavity within the aluminum pipe used for shielding. In addition, there was a considerable savings of time and materials in not having to construct and fill more than 70 sample bulbs which would have been required for this study. Since the gas filling system was kept open to the vapor cell during each run, there was no need to compensate for pressure changes due to variations in temperature of the laboratory or changes in volume due to sealoff. The filling system consisted of a small vacuum line fitted with a mercury manometer which was read with a cathetometer. The buffer gases used in this study were obtained commercially. A number of the buffers were purified before use and analyzed by gas chromatography and mass spectrometry. Details are available elsewhere.²⁰ The inside of the cylindrical Pyrex vapor cell was coated with paraffin to decrease wall relaxation.

In a typical study involving a given buffer gas, four to six observations were made over a range of pressures extending up to 45–65 mm Hg. For each pressure, three hyperfine measurements and two or three Zeeman measurements were recorded. The values of the observed hyperfine and Zeeman frequencies were averaged and the shift, $\Delta\nu$, was calculated from the relationship $\nu = \nu_0 + 7\nu_z + \Delta\nu$ for each buffer gas pressure. Here ν is the observed hyperfine frequency, ν_z is the observed Zeeman frequency, and ν_0 is the unshifted hyperfine frequency ($\nu_0 = 9, 192, 631, 770$ Hz). Line-widths for the hyperfine and Zeeman transitions varied between 700–1100 and 120–150 Hz, respectively, depending upon the buffer gas used.

III. RESULTS

A least-squares analysis was used to make a linear fit of the raw data of $\Delta\nu$ vs P for each buffer. The best estimates of the slope m and its standard error σ_m were used to compute the fps and the standard error in the fps. The least-squares procedures most frequently encountered are based on the assumption that only the dependent variable is subject to error.²¹ In the present case, however, this assumption is suspect since there are errors associated with the measurement of both the independent variable P as well as the dependent variable $\Delta\nu$. For buffers with a large

fps, an uncertainty of ± 0.1 mm represents a serious source of error. Therefore the results were examined in order to determine whether errors in pressure measurement might significantly influence the calculated value of the fps. This was done by performing the least-squares procedure for each buffer a second time, this time taking P as the dependent variable which was subject to error. The slope and its standard error are related in the two cases by²²

$$m = 1/m' \quad \text{and} \quad \sigma_m = m'^2 \sigma_{m'},$$

where the primed quantities refer to the case where P is the dependent variable. The slopes and their standard errors calculated by both methods were identical and it was thus concluded that errors in pressure measurement did not affect these results significantly. In order to make the error limits more realistic, the quantity

$$\Sigma_m = (\sigma_m^2 + m'^4 \sigma_{m'}^2)^{1/2} = \sqrt{2} \sigma_m$$

was taken as the standard error in the slope. In addition, the minimum uncertainty in the fps was taken to be $\pm 0.5 \times 10^{-9}$ Torr⁻¹. The values of the fps and their uncertainties found in this work are listed in Table I,²³ along with values of the fps found by other workers. The temperatures of the present experiments varied between 25 and 28 °C.

Nonrelaxing wall collisions²⁴ can lead to wall shifts which may also affect the fps significantly. Wall shifts become important at low pressures where they cause the measured $\Delta\nu$ values to be systematically shifted by either a positive or negative amount, depending upon the sign of the wall shift. If the wall shifts are large they can introduce curvature in the $\Delta\nu$ -vs- P data at low pressures, thereby affecting the slope and, consequently, the fps. In order to ascertain whether wall collisions had any effect on the measurements of the fps, the deviation of $\Delta\nu$ measured at the lowest-pressure point was compared with that predicted by the least-squares analysis for each buffer gas. When these absolute deviations for each buffer were compared with each other it was found that the deviations were random; roughly half were positive and half were negative, irrespective of whether the buffer caused red shifts or blue shifts in the hyperfine frequency. In addition, the deviations of all measured values of $\Delta\nu$ from the least-squares value predicted for each buffer were examined for curvatures at low pressures, and none were found for any buffer. It was therefore concluded that wall shifts did not have any significant effect on the results.

The values of the fps of neon and argon found in this study corroborate those found by Beatty, Ben-

der, and Chi^{11(c)} while the value found for N_2 agrees with the later work of Arditì and Carver.^{11(b)} The value of the fps of helium lies between that given by Beatty *et al.*^{11(c)} and Arditì and Carver.^{11(b)} The value for the fps of H_2 is less than the value for helium, in keeping with the trend observed for atomic hydrogen and the other alkali metals. In addition, the buffer gases H_2 and D_2 gave the same fps to within experimental error. Bender *et al.* observed similar behavior for the case of ^{87}Rb in atmospheres of H_2 and D_2 .¹⁰ The values of the fps determined in this work for the hydrocarbons and CD_3H differ somewhat from those obtained by Bernheim and Kohuth.^{11(d)} The overall accuracy of their results was given as $\pm 5\%$. While most of our results lie within this limit, the results for methane and ethylene differ by about 12%.

IV. DISCUSSION

The ground-state hyperfine splitting in alkali-metal atoms arises mainly from the Fermi contact interaction of the valence electron

$$\mathcal{H}_F = \frac{2}{3} \pi g_s g_N \beta_e \beta_N \vec{I} \cdot \vec{S} \delta(\vec{r}). \quad (1)$$

The effect of the δ function in Eq. (1) is to make the hyperfine splitting proportional to $|\psi(0)|^2$, the valence-electron density at the nucleus. In the presence of a buffer atom or molecule, the valence-electron density is perturbed, and the resultant change in $|\psi(0)|^2$ is generally considered as arising from a competition between short-range exclusion interactions and long range Van der Waals interactions. The short-range Pauli interactions have the effect of increasing the electron density at the nucleus, producing positive shifts. This contribution can be calculated by Schmidt orthogonalizing the alkali and buffer orbitals to one another and using the orthogonalized wave function to find $|\psi(0)|^2$. Using a perturbation approach Adrian^{15(a)} has shown that the short-range (SR) contribution to the fractional shift from rare-gas buffers can be expressed approximately as

$$\left(\frac{\Delta\nu}{\nu_0}\right)_{\text{SR}} = \frac{|\psi(0, R)|^2 - |\psi(0, \infty)|^2}{|\psi(0, \infty)|^2} = S^2(R), \quad (2)$$

where $|\psi(0, R)|^2$ is the unpaired electron density at the nucleus of the alkali when the buffer is at a distance R and $S(R)$ is the overlap integral of the alkali valence orbital with the outer-shell orbitals of the buffer. The long-range forces act to polarize the orbitals, causing a decrease in the electron density at the nucleus which results in negative shifts. The long-range contribution to the fps can be estimated by subjecting the alkali-buffer system to the perturbation Hamiltonian

$$\mathcal{H} = \mathcal{H}_F + \mathcal{H}_V, \quad (3)$$

where \mathcal{H}_F is given by Eq. (1) and \mathcal{H}_V is the Van der Waals interaction. The lowest-order contribution to the shift occurs at third order and is second order in the Van der Waals interaction and first order in the hyperfine interaction. By using the closure approximation, the long-range (LR) contribution is found to be proportional to the Van der Waals dispersion energy ΔE_V ,^{5(a)}

$$\left(\frac{\Delta\nu(R)}{\nu_0}\right)_{\text{LR}} = \Delta E_V \left(\frac{2}{E_A} + \frac{1}{E_A + E_B}\right), \quad (4)$$

where

$$\Delta E_V = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \dots \quad (5)$$

and E_A and E_B are taken to be the average excitation energies of the alkali and buffer, respectively.^{15(a)} A similar relation but with slightly different energy denominators coming from the closure approximation has been given by Herman and Margenau.^{15(b)} Finally, since both the long- and short-range contributions to the fps depend explicitly upon R , the alkali-buffer internuclear separation, a Boltzmann average must be taken over all alkali-buffer configurations to obtain the average value of the fps which is observed experimentally:

$$\begin{aligned} \text{fps} &= \frac{\partial}{\partial P} \frac{\Delta\nu(R)}{\nu_0} \\ &= \frac{4\pi}{kT} \int_0^\infty \frac{\Delta\nu(R)}{\nu_0} \exp\left(\frac{-V(R)}{kT}\right) R^2 dR, \end{aligned} \quad (6)$$

where $\Delta\nu(R)/\nu_0$ encompasses both the long- and short-range contributions to the fps and $V(R)$ is the alkali-buffer intermolecular potential.

A negative fps is observed experimentally for alkali-metal vapors in heavy buffers such as krypton or xenon, while positive shifts are found with light buffers such as helium or neon. In general, both the long- and short-range contributions increase as the atomic number of the buffer increases, but the long-range contribution eventually dominates, resulting in net negative shifts. A plot of the fps of cesium in rare gas buffers vs C_6 , the coefficient of the leading term in the expansion of the Van der Waals dispersion energy,²³ is given in Fig. 2 and shows this trend quite well. The variation in E_V also dominates the variation of Eq. (4) with different buffer species. It is apparent from Fig. 2 that the saturated hydrocarbons also exhibit a linear dependence of fps vs C_6 except that the shifts are not as negative as those produced by the noble gases. Anisotropic interactions and permanent multipole moments present in the molecular buffers will affect both the short- and long-range

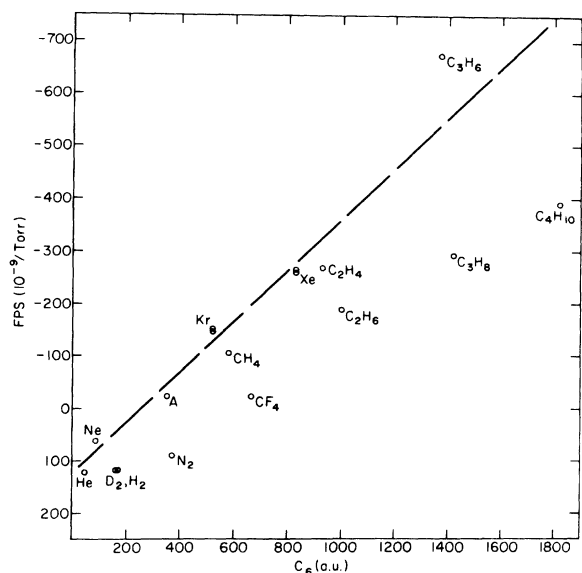


FIG. 2. Cesium fractional pressure shifts as a function of C_6 , the coefficient of the leading term (R^{-6}) of the dispersion energy. The dashed line indicates the almost linear dependence of the fps upon C_6 for the noble gases.

interactions as well as the averaging in Eq. (6) and may be responsible for the deviations from the behavior exhibited by the noble gases. For cylindrically symmetric molecules, the leading term in the Van der Waals dispersion energy becomes, to a good approximation,²⁵

$$\Delta E_V = -(C_6/R^6)[1 + \kappa P_2(\cos\theta)], \quad (7)$$

where κ is a measure of the anisotropy of the molecular polarizability and for many compounds has a value between 0.05 and 0.15. Anisotropic dispersion forces can therefore be expected to cause the long-range contribution to the shift to vary as much as 10–20%, subject to an average over angles. Induction forces, which arise from the interaction of the alkali with the permanent electric moments of the buffer, also contribute to the long-range portion of the shift. Since these forces are attractive, their inclusion tends to make the long-range contribution to the shift more negative.

Turning our attention to specific examples, we notice that the shifts of the two deuterated methanes, CD_3H and CD_2H_2 (not shown in Fig. 2) are slightly more positive than that of methane, with the shift of the triply deuterated species being the more positive. The effect of deuteration is generally to shorten the average bond distances, thus reducing the polarizability and, therefore the long-range contribution to the fps. In addition, the average sizes of the deuterated methanes are

smaller than that of methane, causing the minimum of the alkali-buffer potential to be shifted to smaller R , giving more weight to the positive, short-range contribution to the fps.

The fps due to alkane buffers becomes increasingly negative as C_6 increases but less pronounced than in the case of the noble gases. We may offer several reasons for this trend. First, the anisotropies of the short-range repulsive forces and the short-range contribution to the shift increase with increasing chain size, as is most easily verified by considering space-filling molecular models of the alkanes in their most stable, all-*trans* conformations. Second, the anisotropy parameter κ also increases with chain size, making the long-range forces and their contribution to the fps more anisotropic. Recent measurements of depolarization ratios of the alkanes ethane, propane, and butane give values of κ of 0.076, 0.087, and 0.096, respectively.²⁵ These two effects, when averaged over angles, may be responsible for the observed trends in the alkane shifts. On the other hand, the shifts of the unsaturated buffers ethylene (C_2H_4) and propylene (C_3H_6) show deviations from noble-gas behavior which are much less than those of the corresponding saturated species ethane and propane. Although the anisotropy parameter κ of ethylene²⁶ is larger than that of ethane (0.143 vs 0.076), it may well be that the short-range contribution to the fps of ethylene is much less anisotropic than that of ethane; the π -electron cloud surrounding ethylene would present a more isotropic appearance to the alkali atom than the σ bond in ethane. The fps of propylene is significantly more negative than the saturated hydrocarbons. Recollecting the earlier discussion regarding the long-range portion of the fps, we found that induction forces can increase the long-range contribution, causing the overall shift to become more negative. Recent measurements by Ackermann *et al.*¹² on $^{137}Ba^+$ ions in atmospheres of helium and argon have revealed values for the fps which are much more negative than those of the isoelectronic cesium atom. Ray^{15(h)} has shown theoretically that this can be attributed almost entirely to charge-induced dipole- and charge-induced quadrupole-type induction forces. Since propylene has a dipole moment of 0.34 D, it is quite conceivable that dipole-induced dipole induction forces increase the long-range portion of the shift, leading to a more negative value of the fps than that for the corresponding alkane.

The fps of the diatomic buffers are more positive than would be predicted from the C_6 behavior of the noble gases, which is consistent with a contribution from the anisotropy in the polarizability. There is negligible anisotropy in the long-range

dispersion forces for CH_4 and CF_4 ,²⁷ but the deviations can arise from anisotropies in the short-range forces, which are also used to explain the broadening of the infrared spectrum of methane by the noble gases.²⁸

The present results are in general agreement

with a concept of a fps dominated by long-range Van der Waals interactions for heavy buffer gases. While the effects of anisotropies in the potential are qualitatively present in the data, a more detailed theoretical treatment is needed to determine their exact role.

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²²Reference 21, pp. 119–121.

²³Values of the C_6 dispersion force constant used in Table I and Fig. 2 were obtained as follows: (a) Values of C_6 for the buffers He, Ne, Ar, Kr, Xe, H_2 , N_2 , and CH_4 are those recommended by Dalgarno [*Adv. Chem. Phys.* **12**, 143 (1967)]; (b) The C_6 constants for D_2 , C_2H_6 , C_3H_8 , C_4H_{10} , C_2H_4 , C_3H_6 , and CF_4 were calculated by first using the Slater-Kirkwood formula [see E. W. Rothe and R. B. Bernstein, *J. Chem. Phys.* **31**, 1619 (1959)]. The values of the buffer polarizabilities used in the formula were also taken from Rothe and Bernstein, while the more recent value of the cesium polarizability [P. W. Langhoff and M. Karplus, in *The Padé Approximant in Theoretical Physics*, edited by G. A. Baker, Jr. and J. L. Gammel (Academic, New York, 1970)] was used. Since the values of C_6 of the rare-gas and molecular buffers calculated from the Slater-Kirkwood formula are consistently smaller than the available exact results by 18–28%, we adjusted the Slater-Kirkwood results by multiplying by 1.28 (the amount by which the Slater-Kirkwood result for CH_4 differs from the exact result) to obtain the C_6 constants of D_2 , CF_4 , and the hydrocarbon buffers. Had we used the Slater-Kirkwood results for C_6 consistently for all of the buffers in this study, the appearance of Fig. 2 would have remained unchanged.

²⁴E. N. Bazarov, M. E. Zhabotinsky, V. F. Zolin, and M. E. Samokhina, in *Quantum Electronics*, edited by P. Grivet and N. Bloembergen (Columbia U.P., New York, 1964), pp. 295–297.

²⁵A. Dalgarno, *Adv. Chem. Phys.* **12**, 143 (1967).

²⁶N. J. Bridge and A. D. Buckingham, *Proc. R. Soc. A* **295**, 334 (1966).

²⁷(a) Tetrahedral molecules exhibit anisotropic long-range interactions which vary as R^{-7} and arise from higher-order polarizabilities. See Refs. 25 and 27(b); (b) C. G. Gray, *J. Chem. Phys.* **50**, 549 (1969).

²⁸R. L. Armstrong, S. M. Blumenfeld, and C. G. Gray, *Can. J. Phys.* **46**, 1331 (1968).