Chemical Shift and Relaxation of Xe^{129} in Xenon Gas*

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The density-proportional chemical shift observed by Carr and his associates in xenon gas can be used as a means of calibrating the spin-rotational coupling existing in a diatomic xenon system during collisions of xenon atoms. The basis of this calculation is Ramsey's theory of chemical shifts. The value of the coupling thus obtained is of the correct magnitude to account for the observed relaxation of Xe^{129} in xenon gas.

INTRODUCTION

A DENSITY-proportional chemical shift in the Xe^{129} resonance in xenon gas and liquid has been found by Streever and Carr[1] and, more recently, by Hunt and Carr.[2] Their observations show that this shift from the extreme low-density line is accurately proportional to density over a wide range extending from the rare gas well into the liquid phase. Also, Hunt and Carr[2] working with purer samples than Streever and Carr have found that the relaxation rate T_1^{-1} for Xe^{129} is proportional to the density.

The mechanism for relaxation of Xe^{129} is not finally determined, but Hunt and Carr[2] have evidence that seems to exclude several possibilities. Direct nuclear dipolar interaction is by no means sufficient to account for the observed relaxation rate. There is good evidence that impurities such as O_2 have been reduced to negligible proportions and wall effects can be excluded. The observed independence of T_1 on magnetic field rules out the anisotropic chemical shift mechanism. No Overhauser enhancement of Xe^{129} is produced on saturating the Xe^{131} resonance whereas a 30% enhancement would be expected if the Xe^{129} relaxation is caused by an electron-coupled scalar interaction between the two nuclei during collisions. The absence of such enhancement does not exclude a possible electron-coupled tensor interaction which could be an effective mechanism for collisions between Xe^{129} atoms. However, because of the closed shell electron configurations one would expect the scalar type to dominate.

There remains the possibility that relaxation in Xe^{129} is caused by a spin-rotational coupling existing (a) during atomic collisions or (b) during the transient existence of diatomic molecules. The presence of such molecules in small amounts has been suggested by Bernardes and Primakoff.[3] These two possibilities differ only with respect to the duration of the association of two atoms, since the molecules postulated by Bernardes and Primakoff are bound loosely by Van der Waals forces, the same forces coming also into play during binary collisions.

It is the purpose of this paper to point out that a connection exists between the chemical shift and the spin-rotational coupling constant, this connection being given by Ramsey's[4] theory of chemical shifts. It will be shown that this connection can be used to determine the spin-rotational coupling from the observed chemical shift, and that the relaxation time T_1 calculated from this calibrated coupling is in excellent accord with the observations of Hunt and Carr.[2]

The magnitude of the spin-rotational interaction in xenon gas and its possible role in the relaxation of Xe^{129} spins was theoretically examined originally by Adrian.[5] He concluded that the coupling was insufficiently strong to account for the relaxation. His theory was based on a formula of Wick giving the magnetic field at a nucleus of a diatomic molecule produced by molecular rotation; this same formula, involving a sum over virtually excited states, was also used by Ramsey in his theory of the chemical shift. In Ramsey's theory the same sum occurs in the chemical shift formula and is eliminated between the two to give the direct relationship mentioned above. In Adrian's work the value of the sum is estimated using some rough approximations which give a result a factor of 13 too small to fit the observed chemical shift data. In view of the crudity of the approximations used, the failure of this calculation by an order of magnitude although somewhat disturbing is perhaps understandable.

THE CHEMICAL SHIFT

The diamagnetism of the electrons of an isolated xenon atom provides a substantial chemical shift from the resonant field of a bare nucleus, amounting to about 70 G in a field of 12 000 G. The change in this shift due to association with another xenon atom may be calculated by means of Ramsey's theory[4] of chemical shifts. In Ramsey's expression there appears the so-called paramagnetic term in the form of a sum over virtually excited states. The dichotomy between diamagnetic and paramagnetic contributions is not gauge invariant, although the total shift, of course, is. Using Ramsey's gauge, the paramagnetic term is seen to be closely related to a similar sum over excited states occurring in

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[1] R. L. Streever and H. Y. Carr, Phys. Rev. 121, 20 (1961).
[2] E. R. Hunt and H. Y. Carr, Bull. Am. Phys. Soc. 7, 293 (1962).
[3] N. Bernardes and H. Primakoff, J. Chem. Phys. 30, 691 (1959).
[4] N. F. Ramsey, Phys. Rev. 78, 699 (1950).
[5] F. J. Adrian, thesis, Cornell University, University Microfilms Inc. (1955).

Wick's theory[6] of the magnetic field at a nucleus of a diatomic molecule due to rotation. Eliminating the excited state sum between the two expressions, Ramsey arrives at the result

$$\sigma = (e^2/3mc^2)\langle 0|\sum_k 1/r_k|0\rangle + (e/3mc\omega)(H_r - Ze\omega/cR). \quad (1)$$

Here, r_k is the distance of the kth electron from the nucleus for which the shift is being calculated and the sum is over the electrons of both atoms. H_r is the magnetic field at that nucleus due to rotation of the diatomic system, ω is the angular velocity of the line of centers, Z is the atomic number and R the internuclear separation. Equation (1), as shown by Ramsey, does not depend on the perturbation theory used in its derivation, but can be obtained on more exact grounds.

In order to compute the shift observed by Carr,[1,2] one must first find $\Delta\sigma$, the difference between (1) and the σ of an isolated xenon atom. This $\Delta\sigma$ is the instantaneous shift and the observed shift is found by taking an appropriate statistical or kinetic average of $\Delta\sigma$.

In the first term of (1) we separate the $\sum_k$ into sums over atom A at whose nucleus the shift is being evaluated and over the other atom B. For the latter part we expand as follows:

$$1/r_k = (1/R)\sum_{n=0}^{\infty} (r_k'/R)^n P_n(\cos\theta_k'), \quad (2)$$

where r_k', θ_k' are coordinates of electron k at atom B relative to nucleus B. We may now rewrite (1) as

$$\sigma \cong (e^2/3mc^2)\langle 0|\sum_k{}^A 1/r_k|0\rangle + (e^2/3mc^2)(Z/R)$$

$$+ (e^2/3mc^2R^2)\langle 0|\sum_k{}^B r_k'\cos\theta_k'|0\rangle$$

$$+ (e^2/3mc^2R^3)\langle 0|\sum_k{}^B r_k'^2 P_2(\cos\theta_k')|0\rangle$$

$$+ eH_r/3mc\omega - Ze^2/3mc^2R. \quad (3)$$

In this expression the second term cancels with the last term, and the third term vanishes by symmetry considerations.[7] The fourth term is very small. Its value has been estimated, using a Slater-Kirkwood wave function for the ground state, to be 2×10^{-11}. Neglecting this small term, we are left with the first and fifth terms. From this result we must now subtract the diamagnetic shift of an isolated atom and finally obtain for $\Delta\sigma$,

$$\Delta\sigma = (e^2/3mc^2)\{\langle 0|\sum_k{}^A 1/r_k|0\rangle - \langle 0|\sum_k{}^A 1/r_k|0\rangle_0\}$$

$$+ eH_r/3mc\omega. \quad (4)$$

In the first term, the subscript 0 means that the wave

function of the isolated atom must be used. In order to estimate the order of magnitude of the first term we shall neglect the exchange forces and take for the perturbed wave function of the diatomic system a Slater-Kirkwood function[8,9]

$$\varphi = \psi_0(1+v)/[1+(v^2)_{00}]^{1/2} \quad (5)$$

where ψ_0 is the ground state wave function of the unperturbed system and

$$v = \sum_{ij} \lambda_{ij}(x_i\zeta_j + y_i\eta_j - 2z_i\xi_j). \quad (6)$$

In (6), (x_i,y_i,z_i) is the position vector of the ith electron of atom A and (ζ_j,η_j,ξ_j) that of the jth electron of atom B each referred to the respective nucleus and both z_i and ξ_j are measured along the line of centers. λ_{ij} are variation parameters and $(v^2)_{00}$ is the expectation value of v^2 for the unperturbed system. Restricting the sums in (6) to the outer shell electrons all λ_{ij} are equal and have the common value[9]

$$\lambda = (e^2m\alpha/4N_0\hbar^2R^6)^{1/2}, \quad (7)$$

where α is the polarizability of a xenon atom and $N_0(=6)$ is the number of outer shell electrons. Assuming ψ_0 is a simple product wave function one finds for the expression in the curly brackets in Eq. (4)

$$\beta = -\tfrac{2}{3}\lambda^2 N_0^2\langle r^2\rangle_{\mathrm{av}}(\langle r^2\rangle_{\mathrm{av}}/\langle r^{-1}\rangle_{\mathrm{av}} - \langle r\rangle_{\mathrm{av}}), \quad (8)$$

where the averages are over the unperturbed wave function. We are interested only in the order of magnitude and so will neglect $\langle r\rangle_{\mathrm{av}}$ and put[9]

$$\langle r^2\rangle_{\mathrm{av}} = 3(\hbar^2\alpha/4N_0me^2)^{1/2}. \quad (9)$$

Using (7) we then get

$$-\beta \simeq (3\alpha^2/8R^2)\cdot\langle r^{-1}\rangle_{\mathrm{av}}. \quad (10)$$

Putting[9] $\alpha = 4\times10^{-24}$ cm³, $R = 4\times10^{-8}$ cm, and $\langle r^{-1}\rangle_{\mathrm{av}} = 10^{+8}$ cm⁻¹, we find for the first term of (4)

$$(\Delta\sigma)_1 = -1.4\times10^{-8}. \quad (11)$$

This is entirely negligible compared either to the experimental value of $\Delta\sigma$ (inferred from Hunt and Carr's data[2]) of -3.8×10^{-5} or to the theoretical value of the second term of (4) based on Adrian's[5] estimate of H_r: $(\Delta\sigma)_2 = -3\times10^{-6}$. We, therefore, neglect the first term of (4) and arrive at the very simple result

$$\Delta\sigma = (e/3me\omega)H_r. \quad (12)$$

Quite generally H_r will be proportional to ω, the proportionality factor depending only on R. That is,

$$H_r = \omega f(R), \quad (13)$$

giving

$$\Delta\sigma = (e/3mc)f(R). \quad (14)$$

[6] G. C. Wick, Phys. Rev. **73**, 51 (1948).
[7] This is certainly the case if the interaction between the atoms is of the dispersion type. In any case it is negligibly small.

[8] J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).
[9] H. Margenau, Rev. Mod. Phys. **11**, 1 (1939).

We must now make a suitable statistical or kinetic average of (14). The proper statistical average is obtained by integrating (14) over the radial density function. For low densities

$$\langle\Delta\sigma\rangle_{\text{av}} = (e/3mc)\int e^{-u(R)/kT}f(R)N4\pi R^2 dR, \quad (15)$$

where N is the number density of atoms and $u(R)$ the interaction potential. The rigid-sphere model,

$$u(R) = \infty, \quad R < R_m$$
$$= 0, \quad R > R_m \quad (16)$$

gives

$$(\langle\Delta\sigma\rangle_{\text{av}})_{\text{r.s.}} = (4\pi eN/3mc)\int_{R_m}^{\infty} f(R)R^2 dR. \quad (17)$$

The Lennard-Jones potential

$$u(R) = 4\epsilon[(a/R)^{12} - (a/R)^6] \quad (18)$$

gives

$$(\langle\Delta\sigma\rangle_{\text{av}})_{\text{LJ}}$$
$$= \frac{4\pi eNa^3}{9mc}\int_0^{\infty} \exp[-\gamma s^2(s^2-1)]f(as^{-1/3})\frac{ds}{s^2}, \quad (19)$$

where $\gamma \equiv 4\epsilon/kT$.

From (17) and (19) we see that measurements of $\langle\Delta\sigma\rangle_{\text{av}}$ do not determine H_r directly, but only certain integrals of H_r over R. In order to obtain a useful result that can be inserted in the theory of relaxation, some form for the function $f(R)$ must be assumed.

It may be expected that $f(R)$ will be a rapidly decreasing function of R. It will suffice to take $f(R) = KR^{-n}$. Assuming some value for n, the constant K can be determined from the shift data and then used to find a value for T_1, If exchange forces are neglected so that only Van der Waals interactions are included one finds[5] $n=6$. For definiteness we shall assume this value for n although the final result will not depend critically on the value of n assumed. With $n=6$ we get from the rigid-sphere model [Eq. (17)]

$$(\langle\Delta\sigma\rangle_{\text{av}})_{\text{r.s.}} = 4\pi eNK/9mcR_m^3, \quad (20)$$

and from the Lennard-Jones potential, taking[10] $\epsilon = 319\times10^{-16}$ ergs and $T = 298°$K,

$$(\langle\Delta\sigma\rangle_{\text{av}})_{\text{LJ}} = 1.672(4\pi/9)(eNK/mca^3). \quad (21)$$

If in (21) we put[10] $a = 3.94\times10^{-8}$ cm and for K, Adrian's result,[5] -2.1×10^{-57} cgs units we obtain $\langle\Delta\sigma_{\text{exp}}\rangle = -3.3\times10^{-8}$ per amagat.

This is to be compared to Hunt and Carr's result,[2]

$$(\langle\Delta\sigma\rangle_{\text{av}})_{\text{exp}} = -4.2\times10^{-7} \text{ per amagat.} \quad (23)$$

[10] G. K. Horton and J. W. Leech, Proc. Phys. Soc. (London) (to be published).

RELAXATION TIME

In computing the relaxation time one has the option (as in the case of $\Delta\sigma$) of using either a kinetic (time) average or a statistical (ensemble) average. Each procedure has its advantages. The kinetic average is the simplest in the low-density case for collision dynamics based on the rigid-sphere model, but becomes almost unmanageable for more realistic models and at higher densities. The statistical average, although manageable for realistic potentials, must be based at present on the approach of Oppenheim and Bloom[11] which involves "the constant acceleration approximation." Although this approximation is probably a good one, its reliability has not yet been adequately tested.

We shall first calculate T_1 for the low-density case using a kinetic average with the rigid-sphere model. Later we shall discuss the application of the Oppenheim-Bloom theory to this problem.

Consider a Xe^{129} atom moving through the gas and making random collisions. The very small probability of a nuclear spin flip as a result of a single collision is, by perturbation theory,

$$W = \hbar^{-2}\left|\int_{-\infty}^{+\infty} \mathcal{H}'(t)e^{-i\omega_0 t}dt\right|^2. \quad (24)$$

Here, $\omega_0 = \gamma H_0$ is the Larmor frequency in the large steady field H_0 and $\mathcal{H}'$ is the interaction Hamiltonian

$$\mathcal{H}' = -\gamma\hbar\mathbf{I}\cdot\mathbf{H}_r. \quad (25)$$

An alternative expression for $\mathcal{H}'$ is obtained from (13) noting that

$$\boldsymbol{\omega} = \mathbf{R}\times\mathbf{P}/\mu R^2$$

where the relative momentum $\mathbf{P} = \mu\mathbf{V}_r$, μ is the reduced mass, and $\mathbf{V}_r$ the relative velocity. Thus,

$$\mathcal{H}' = -(\gamma\hbar/\mu R^2)f(R)\mathbf{I}\cdot\mathbf{R}\times\mathbf{P}. \quad (26)$$

Since $\mathcal{H}'(t)$ is a very sharp function of time, the limits of integration in (24) have been taken from $-\infty$ to $+\infty$. For the same reason the factor $e^{-i\omega_0 t}$ may be replaced by unity. Thus, from (25) we obtain

$$W = \tfrac{1}{4}\gamma^2\left|\int_{-\infty}^{+\infty} H_r(t)dt\right|^2 \sin^2\theta, \quad (27)$$

where θ is the angle between $\mathbf{H}_r$ and $\mathbf{H}_0$. Since $\mathbf{H}_r$ is orthogonal to the orbital plane, θ is constant during a collision. We may anticipate subsequent averaging over collisions by replacing $\sin^2\theta$ by its average over the unit sphere of $2/3$, obtaining

$$W = \tfrac{1}{6}\gamma^2\left|\int_{-\infty}^{+\infty} H_r(t)dt\right|^2. \quad (28)$$

[11] I. Oppenheim and M. Bloom, Can. J. Phys. 39, 845 (1961).

The probability w, per unit time, that the Xe[129] nucleus flips is then given by averaging W over the collision frequency. Let $n(V_r)dV_r$ be the number of atoms per unit volume with velocity relative to the given atom of V_r in dV_r and b be the impact parameter of a collision; then

$$w = \int_0^\infty \int_0^\infty W \times 2\pi n(V_r)dV_r \, V_r b \, db \qquad (29)$$

and

$$N = \int_0^\infty n(V_r)dV_r. \qquad (30)$$

We find at once for $1/T_1 = 2w$

$$1/T_1 = (2\pi/3)\gamma^2 \int_0^\infty n(V_r)V_r dV_r$$

$$\times \int_0^\infty b\,db \left(\int_{-\infty}^{+\infty} H_r dt\right)^2. \quad (31)$$

In order to extract a value of T_1 from this expression, it is necessary to consider the dynamics of a collision. We shall return to this matter in a moment, but first let us note that $\Delta\sigma$ of Eqs. (12) or (14) might have been averaged over collisions in a manner similar to $1/T_1$. In fact, such an average gives

$$\langle\Delta\sigma\rangle_{av} = (2\pi e/3mc)\int_0^\infty n(V_r)V_r dV_r$$

$$\times \int_0^\infty b\,db \int_{-\infty}^{+\infty} f[R(t)]dt. \quad (32)$$

This expression can be transformed by (a) putting $d\varphi = \omega dt$ so that φ is the angle of the internuclear axis with the respect to the original relative velocity and (b) putting $bV_r = \omega R^2$, because of angular momentum conservation.[12] We, then, obtain

$$\langle\Delta\sigma\rangle_{av} = (2\pi e/3mc)\int_0^\infty h(V_r)dV_r$$

$$\times \int_0^\infty db \int_0^{\varphi\infty} R^2 f(R)d\varphi. \quad (33)$$

It is instructive to verify that this expression agrees with the statistical average of Eq. (17). For the rigid-sphere model the integrals over φ and b do not depend on V_r so

$$\langle\Delta\sigma\rangle_{av} = (2\pi eN/3mc)I,$$

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[12] Because of the very large angular momentum in a collision, the classical approximation in the collision dynamics suffices and it is unnecessary to take account of a possible transfer of angular momentum $\hbar$ to a nucleus.

where

$$I = \int_0^\infty db \int_0^{\varphi\infty} R^2 f(R)d\varphi$$

$$= 2\int_0^{R_m} db \int_0^{\varphi_0} R^2 f(R)d\varphi + \int_{R_m}^\infty db \int_0^\pi R^2 f(R)d\varphi,$$

where $R_m \equiv b\sin\varphi_0$ and φ_0 is the value of φ on impact. Also, since $\sin\varphi = b/R$, $d\varphi = -bdR/(R^2-b^2)^{1/2}$ and so

$$I = 2\int_0^{R_m} db \int_{R_m}^\infty Rf(R)b(R^2-b^2)^{-1/2}dR$$

$$+ 2\int_{R_m}^\infty db \int_b^\infty Rf(R)b(R^2-b^2)^{-1/2}dR. \quad (34)$$

In the first integral we reverse the order of integration and in the second we integrate by parts and find that (34) reduces to

$$I = 2\int_{R_m}^\infty R^2 f(R)dR. \qquad (35)$$

Inserting (35) in (33) we obtain Eq. (17), verifying the identity of the statistical and kinetic averages in this case.

Returning now to Eq. (31) for $1/T_1$ and putting $dt = -d\varphi/w$, $H_r = \omega f(R)$, we get

$$1/T_1 = \tfrac{2}{3}\pi\gamma^2 \int_0^\infty n(V_r)V_r dV_r$$

$$\times \int_0^\infty b\,db \left(\int_0^{\varphi\infty} f(R)d\varphi\right)^2. \quad (36)$$

To proceed further we must assume a form for $f(R)$. For reasons mentioned in Part II we take $f(R) = KR^{-6}$.

In the Appendix it is shown that for the rigid-sphere model,

$$\int_0^\infty b\,db \left(\int_0^{\varphi\infty} R^{-6}d\varphi\right)^2 = \frac{7}{45}R_m^{-10}. \qquad (37)$$

Also,

$$\int_0^\infty n(V_r)V_r dV_r = N\bar{V}_r,$$

where

$$\bar{V}_r = (8kT/\pi\mu)^{1/2} \qquad (38)$$

is the mean relative velocity. Thus, we obtain finally for T_1 for the rigid-sphere model and $f(R) = KR^{-6}$,

$$1/T_1 = (14\pi/135)\gamma^2 \bar{V}_r NK^2/R_m^{10}. \qquad (39)$$

Eliminating K between (20) and (39) we get an equa-

tion of the Korringa type

$$T_1(\langle\Delta\sigma\rangle_{av})^2 = \frac{40\pi}{21}\frac{e^2 R_m^4 N}{m^2 c^2 \gamma^2 \bar{V}_r}. \tag{40}$$

In order to evaluate the right member of (40) one must assume a value for R_m, the effective rigid-sphere atomic diameter. It is probably incorrect to take $R_m = a$, the value of R at which the Lennard-Jones potential vanishes. A better procedure is to compare Eqs. (20) and (21). Equating these, we find

$$R_m = a/(1.672)^{1/3}. \tag{41}$$

Inserting (41) in (40) we get

$$T_1(\langle\Delta\sigma\rangle_{av})^2 = 3.56\times10^{-8} \text{ per amagat.} \tag{42}$$

Using Hunt and Carr's latest data,[13] $T_1^{-1} = (5.0\pm0.5)\times10^{-6} \text{ sec}^{-1}\text{ amagat}^{-1}$ and $\langle\Delta\sigma\rangle_{av} = (4.22\pm.05)\times10^{-7} \text{ amagat}^{-1}$, we get

$$[T_1(\langle\Delta\sigma\rangle_{av})^2]_{exp} = 3.6(\pm0.4)\times10^{-8} \text{ per amagat.} \tag{43}$$

The remarkable agreement between (42) and (43) is, of course, largely fortuitous because of the theoretical approximations made.

DISCUSSION

We have shown that the measurements on the chemical shift of Xe^{129} in xenon gas can be used as a calibration of the local field at a Xe^{129} nucleus due to the rotating diatomic system in an atomic collision and that the local field so determined accounts well for the observed relaxation time.

The possibility of determining H_r from the shift data rests on the validity of Eq. (12). This equation has been justified by the use of Ramsey's formula (1) and the neglect of certain terms in the resulting Eq. (3). The neglect of these terms is rendered plausible by an order of magnitude estimate of them. The terms neglected are estimated to be several orders of magnitude smaller than the observed $\Delta\sigma$. The final term included, however, has a theoretical value smaller than the observed $\Delta\sigma$ by one order of magnitude [see Eqs. (22) and (23)]. This discrepancy is disturbing and points to the desirability of a more refined calculation of the local field, H_r.

Nevertheless, there seems little doubt that the spin-rotational coupling is the effective mechanism for the relaxation of Xe^{129} in the gas. Unlike relaxation which can be produced by a variety of mechanisms, the chemical shift can only be due to the distortions of the electron clouds in collisions. Thus, the calibration of H_r by this shift seems unambiguous.

The closeness of the agreement noted between experimental and theoretical values of $T_1(\langle\Delta\sigma\rangle_{av})^2$ is probably

fortuitous. By taking $H_r = KR^{-6}$ we have neglected overlap forces which are especially effective in close collisions. However, generalizing to $H_r = KR^{-n}$ does not affect the order of magnitude of the theoretical $T_1(\langle\Delta\sigma\rangle_{av})^2$ for n considerably larger than 6 (see Appendix). Another source of inaccuracy is the fact that Eq. (40) is based on the rigid sphere model in the collision dynamics. Some mitigation of this error is obtained by use of Eq. (41) for R_m. This effectively small value of R_m does not imply that atoms get that close together during a collision but rather it takes account of a longer time of association resulting from the attractive part of the interatomic potential. This way of including a realistic force law is, however, not very satisfactory. It would be much better to include such a realistic potential in the calculation of T_1 from the start.

The Oppenheim-Bloom theory[11] of relaxation in fluids provides a way of doing this. Recently Oppenheim and Bloom[14] have inaugurated such a calculation by the use of the interaction Hamiltonian of the form (26) in their formalism. We have been able to show that their theory leads to a result for T_1 which for a realistic potential can be determined by machine calculation. We have also shown that for the rigid sphere model their equations gives a result for T_1 which differs from (39) by only 13%. This small difference which is presumably due to their use of the "constant acceleration approximation" shows that at least in this case this approximation is reliable and lends support to its use in the more general case.

We have based our calculations on the assumption that xenon gas is monatomic. Bernardes and Primakoff[3] have shown theoretically that diatomic xenon molecules bound by van der Waals forces may exist in small percentages in xenon gas. The possible presence of such molecules suggests that the mechanism involved here for relaxation might prove to be more effective than in a monatomic gas because of the longer times of association of a diatomic system. We now present a rough calculation to show that such molecules in small percentages would be less effective than atomic collisions in producing relaxation.

First assuming no molecules and only atomic collisions, let us assume that H_r is constant for a time τ_c of a collision and vanishes outside that time. The Eq. (28) gives $W = \frac{1}{6}\gamma^2 H_r^2 \tau_c^2$. If τ_0 is the mean time between collisions, we get for T_1

$$1/T_1 = \frac{1}{6}\gamma^2 H_r^2 \tau_c^2/\tau_0.$$

On the other hand, by Eq. (12)

$$\langle\Delta\sigma\rangle_{av} = (\rho/3mc)(H_r/\omega)(\tau_c/\tau_0)$$

assuming some mean value for ω during a collision. These two equations give

$$T_1\langle\Delta\sigma\rangle_{av}^2 \cong \frac{2}{3}(e/mc\gamma)^2\omega^{-2}\tau_0^{-1}. \tag{44}$$

[13] E. R. Hunt and H. Y. Carr, preceding paper, Phys. Rev. 130, 2302 (1963).

[14] I. Oppenheim and M. Bloom (private communication).

Let us now assume on the contrary that only during molecular associations are significant shifts and flippings produced.

The calculation is similar to the atomic case with τ_c replaced by the mean time of a continuous molecular association and τ_0 by τ_m, the mean time spent by a xenon atom between molecular associations. Then

$$T_1\langle\Delta\sigma\rangle_{\mathrm{av}}{}^2 = \tfrac{2}{3}(e/mc\gamma)^2\omega^{-2}\tau_m{}^{-1}. \tag{45}$$

By the equipartition therorem, the quantities ω^2 will be about the same in (44) and (45). Expression (45) will hold if relaxation of xenon atoms and their shifts are caused by their transient existence in molecules and if the number of molecules is small compared to the number of atoms. Now we have shown by a more refined calculation that the right side of Eq. (44) is in accord with experiment. Since $\tau_m\gg\tau_0$ it follows that the right side of (45) is very much smaller than the experimental value. We conclude from this argument that even if such molecules exist they cannot be responsible for the observed relaxation and shift.

Our calculations have been based on the assumption of low density. Now it is a fact that at all the densities used by Carr and his associates, the gas is far from ideal. However, although the pressure and density are not linearly related it is a remarkable fact that both T_1^{-1} and $\langle\Delta\sigma\rangle_{\mathrm{av}}$ are within the limits of error proportional to the density. Indeed, in the case of $\langle\Delta\sigma\rangle_{\mathrm{av}}$ this proportionality extends well into the liquid phase. In making statistical evaluations of these quantities, they are integrated over the radial density function which has a "virial expansion" in the density ρ:

$$g(r,\rho) = g_0(r)\rho + g_1(r)\rho^2 + \cdots .$$

If only the first term of this expansion is included, as in (15), one obtains a density-proportional result. If higher terms were important in this averaging they would show up as deviations from linearity of the observed T_1^{-1} and $\langle\Delta\sigma\rangle_{\mathrm{av}}$. Since such effects are not observed, we conclude that the lowest virial term suffices for these quantities, if not for the pressure; not only for the "rare gas," but also in the highly compressed gas and for $\langle\Delta\sigma\rangle_{\mathrm{av}}$ in the liquid. Of course, T_1^{-1} has to be calculated on a different basis for the liquid and this remains an outstanding problem. The independence[13] of T_1 on temperature for liquid xenon is a striking experimental result which needs elucidation.

ACKNOWLEDGMENTS

APPENDIX

We shall prove Eq. (37) of the text. We shall treat the more general case of $H_r = KR^{-n}$ and evaluate

$$J_n = \int_0^\infty b\,db\left(\int_0^{\varphi_0} R^{-n}d\varphi\right)^2 = 4(J_n' + J_n''), \tag{A1}$$

where

$$J_n' = \int_0^{R_m} b\,db\left(\int_0^{\varphi_0} R^{-n}d\varphi\right)^2$$

$$= R_m^{-2n+2}\int_0^{\pi/2} \cos\varphi_0 \sin^{-2n+1}\varphi_0 d\varphi_0\left(\int_0^{\varphi_0} \sin^n\varphi\,d\varphi\right)^2,$$

using

$$b = R\sin\varphi = R_m\sin\varphi_0,$$

and

$$J_n'' = \int_0^\infty b\,db\left(\int_0^{\pi/2} R^{-n}d\varphi\right)^2$$

$$= [1/(2n-2)R^{2n-2}]\left(\int_0^{\pi/2} \sin\varphi\,d\varphi\right)^2. \tag{A2}$$

By a partial integration, J_n' becomes

$$J_n' = [1/(n-1)R^{2n-2}]$$

$$\times \int_0^\infty \sin^{n-2}\varphi_0 d\varphi_0\int_0^{\varphi_0} \sin^n\varphi\,d\varphi$$

$$- [1/(2n-2)R_m^{2n-2}]\left(\int_0^{\pi/2} \sin^n\varphi\,d\varphi\right)^2. \tag{A3}$$

Inserting (A2) and (A3) in (A1), we get

$$J_n = 4B_n/(n-1)R^{2n-2}, \tag{A4}$$

where

$$B_n \equiv \int_0^{\pi/2} \sin^{-n-2}\varphi_0 d\varphi_0 \int_0^{\varphi_0} \sin^n\varphi\,d\varphi. \tag{A5}$$

Changing variables of integration to

$$z = \sin\varphi_0, \quad w = \sin\varphi/\sin\varphi_0,$$

we obtain

$$B_n = \int_0^1\int_0^1 \frac{z^3 dz\,w^n dw}{[(1-z^2)(1-z^2w^2)]^{1/2}};$$

and integrating with respect to z, we get

$$B_n = \frac{1}{2}\int_0^1 w^{n-2}[(w+w^{-1})\tanh^{-1}w - 1]dw.$$

Using the expansion

$$\tanh^{-1}w = \sum_{k=0}^\infty w^{2k+1}/(2k+1),$$

and integrating term by term, we get

$$2B_n = \sum_{k=0}^{\infty} (2k+1)^{-1}(2k+n-1)^{-1}$$

$$+\sum_{k=0}^{\infty} (2k+1)^{-1}(2k+n+1)^{-1} - 1/(n-1).$$

These sums may be expressed in terms of the logarithmic derivative of the gamma function,

$$\psi(x) = -C + \sum_{\nu=1}^{\infty} x/\nu(x+\nu),$$

and we get

$$2B_n = [1/(n-2)][\psi(n-2) - \tfrac{1}{2}\psi(n/2-1) + C/2]$$
$$+ (1/n)[\psi(n) - \tfrac{1}{2}\psi(n/2) + c/2] - 1/(n-1).$$

This result may be expressed as

$$B_n = \frac{n-1}{n(n-2)}\left(\tfrac{1}{2}+\tfrac{1}{4}+\cdots+\frac{1}{n-3}+\ln 2\right) - \frac{1}{2n}, \quad (n \text{ odd})$$

$$= \frac{n-1}{n(n-2)}\left(1+\tfrac{1}{3}+\cdots+\frac{1}{n-3}\right) - \frac{1}{2n}. \quad (n \text{ even})$$

For $n=6$, we find $B_6 = 7/36$ and $J_6 = 7/45R_m^{10}$.

Rotational Excitation and Electron Relaxation in Nitrogen*

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Using the expression given by Gerjuoy and Stein for the cross section for excitation of rotational states in N_2 by monoenergetic electrons, an exact expression for the average electron energy loss rate, $\langle dW_e/dt \rangle$, is derived in the case of a Maxwellian velocity distribution. The results are used in the interpretation of cross-modulation experiments performed at microwave frequencies in an afterglow discharge. Computed results are presented for several gas temperatures, T, in the range 300–735°K with the electron temperature, T_e, being a running variable within 250°K of the gas temperature. It is seen that $\langle dW_e/dt \rangle$ varies linearly with $(T_e - T)$, when T_e is less than 10% in excess of T; and that the slope, proportional to the inverse electron relaxation time, τ, decreases as $T^{-1/2}$. This is also predicted by an approximate, closed form representation of $\langle dW_e/dt \rangle$, which agrees extremely well with the exact computation. The experimental data on τ, found by microwave cross-modulation techniques, agree well with theory. Using Pack and Phelps' relationship between the electron momentum transfer collision frequency ν_m, and T_e, it is found that the G factor varies at $T_e^{-3/2}$, with $G/G_{classical}$ ranging from 55.9 at 300°K, to 14.3 at 735°K.

INTRODUCTION

A S has been suggested by Gerjuoy and Stein[1] two different approaches are feasible in order to compare the theoretically predicted cross section for rotational excitation with experimental results obtained from swarm experiments. The first approach, recently utilized by Frost and Phelps,[2] solves the Boltzmann equation with the rotational excitation terms included; and a reiteration procedure determines the collision cross sections that yield the closest fit to the presently available data on transport coefficients. In this paper, we present a second approach which is based on the cross-modulation phenomenon taking place during the afterglow of a transient, quiescent nitrogen plasma.[3] The electrons, being close to thermal equilibrium with the gas molecules, can be expected to obey a Maxwellian velocity distribution. Thus, an average value of the electron energy-loss rate can be computed and compared directly with observed data on the electron relaxation time, τ. This will also serve the purpose of determining the validity of the assumptions used for the cross-modulation experiment, namely, that the average electron energy-loss rate, $\langle dW_e/dt \rangle$, is proportional to the excess electron energy, $T_e - T$, T being the gas temperature.

Of particular interest, to many workers in the field of plasma diagnostics and ionospheric research, is the fractional electron excess energy loss factor, or the G factor. Apart from the cross-modulation phenomenon, which can be used as a diagnostic tool, substantial microwave heating of the electrons is often desired. In the case of the noble gases, the electron temperature for a specified field strength can be computed, since the G factor is constant (i.e., independent of the electron temperature.) In molecular gases, this is far from being the case and it is one of the purposes of the work reported here to find how the G factor varies with T_e.

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[3] M. Mentzoni, C. Montgomery, and R. Row, Bull. Am. Phys. Soc. **7**, 636 (1962).