with the results of some previous investigators. Estimates of the uncertainty for $N=3$, 4, and even 5 are very difficult to make, as $(Z-s^{(N)})$ in these cases is less than unity. For the higher $N$, the values may be as much as 1 eV too low because of the large, negative, inaccurate $\alpha_4^{(N)}$ values.[24] The perturbation procedure is quite unsuited for the investigation of negative ions, so it is unfortunate, as Edlén remarks,[3] that probably the only practicable extrapolation procedure in this connection is an isoelectronic one.

The data of Johnson and Rohrlich, when account is taken of their *ad hoc* multiplicative factor, and the data of Edlén both fall within the limits set above, as they must, since the present method of estimation furnishes the maximum information permitted from the available ionization energies.

## ACKNOWLEDGMENTS

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[24] The situation is aggravated by the fact that summing the perturbation series through fourth order resulted, for all $N$, in a further arithmetic loss of significant figures due to the positive and negative terms nearly cancelling.

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# Effect of Matrix Interactions and Buffer Gases on the Atomic Nitrogen Hyperfine Splitting*†

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Electron spin resonance studies of trapped nitrogen atoms show that the matrix interaction increases the hyperfine splitting by some 10 to 20% of the free atom value of 10.45 Mc/sec. A similar increase in the hyperfine splitting is produced by buffer gases used in optical spin-polarization studies of nitrogen atoms. These effects can be accounted for by van der Waals interactions between the trapped atom and the matrix or buffer gas particles. These interactions introduce $(2s)(2p)^4$ excited states into the nitrogen wave function. Since the $2p$ shell of the $^4S$ nitrogen atom already contains three electrons with the same spin, only that $2s$ electron with opposite spin can be excited. This increases the unpaired electron density at the nucleus. An approximate calculation of this effect, carried out using perturbation theory, is in qualitative agreement with the experimental results. The magnitude of the effect is proportional to the polarizability of the matrix or buffer gas particle, so that the hyperfine splitting increases with the size of the perturbing species.

## INTRODUCTION

Electron spin resonance (ESR) studies of nitrogen atoms trapped at liquid helium temperature in inert gas matrices[1,2] have shown that the interaction of the nitrogen atom with its surroundings increases the nitrogen hyperfine splitting (hfs) constant by some 10 to 20% of the free atom value of 10.45 Mc/sec.[3] More recently, a spin-exchange optical polarization method has been used to determine the pressure shifts of the nitrogen hyperfine splitting in various buffer gases.[4] The results of these two experiments are in qualitative agreement.

Effects of this type have been observed previously for hydrogen atoms and for alkali atoms in both inert solids[5,6] and in the gas phase.[7] The matrix and pressure shifts in nitrogen are, however, somewhat different from the shifts found for hydrogen and the alkali atoms, as might be expected from the difference in atomic structure between the two types of atoms. Specifically, the matrix and pressure shifts always increase the nitrogen hyperfine splitting, while the hydrogen and alkali atom shifts are sometimes positive and sometimes negative.

In this paper we shall make an approximate calculation of the matrix and pressure shifts of the nitrogen hyperfine splitting following an earlier treatment of the hydrogen atom.[8] In the hydrogen atom the matrix perturbation was assumed to be a combination of van der Waals and exchange forces. It was found that the

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[5] S. N. Foner, E. L. Cochran, V. A. Bowers and C. K. Jen, J. Chem. Phys. **32**, 963 (1960).

[6] C. K. Jen, V. A. Bowers, E. L. Cochran, and S. N. Foner, Phys. Rev. **126**, 1749 (1962).

[7] L. W. Anderson, F. M. Pipkin and J. C. Baird, Jr., Phys. Rev. Letters **4**, 69 (1960).

[8] F. J. Adrian, J. Chem. Phys. **32**, 972 (1960).

former tended to decrease the hydrogen atom hyperfine splitting, while the latter tended to increase the splitting. The competition between these two effects accounted for the occurrence of both positive and negative shifts in the hfs constant, and also explained the fact that heavy buffer gases (e.g., argon) with a large van der Waals interaction produced negative shifts, while light buffer gases (e.g., helium and neon) gave positive shifts.[7] In the nitrogen atom qualitative arguments indicate that the exchange forces make only a minor contribution to the hfs shift, and van der Waals interactions are found to increase the hyperfine splitting for this atom. Thus, the hfs constant of the perturbed nitrogen atom is expected to be greater than the free atom value.

## THEORY

As mentioned in the introduction we shall assume that the interaction between the nitrogen atom and a spherical nonpolar matrix or buffer gas particle may be described as the combination of an exchange interaction and a van der Waals interaction. The exchange or Pauli exclusion forces restrain two electrons of the same spin from occupying the same region of space. Thus, the general tendency of the exchange forces is to cause the wave functions of the interacting species to contract so as to reduce the overlap of the interacting charge clouds. In the case of the hydrogen and alkali atoms where the unpaired electron is in an $s$ orbital this contraction increases the charge density at the nucleus with a consequent increase in the hyperfine splitting.

In the nitrogen atom the situation is different because the unpaired electrons are in $p$ orbitals. When the nitrogen atom is symmetrically surrounded by the matrix particles as in a solid, the exchange forces will contract the $p$ orbitals in a symmetric fashion so that their charge density at the nitrogen nucleus remains zero. In the gas phase where the net perturbation of the nitrogen atom is the average of a number of individual collisions it is possible to have an unsymmetrical exchange perturbation of the $p$ orbitals which will admix a small amount of $s$-state in the form of nitrogen $3s$, $4s$ orbitals, etc. with the $2p$ orbital. However, this effect is expected to be smaller than the contribution of the relatively long-range van der Waals forces which can both excite the $2p$ electrons into higher $s$ orbitals and also produce excitation of the closed shell $2s$ electrons, i.e., $(2s)^2(2p)^3 \rightarrow (2s)(2p)^4$. In such excited states only that $2s$ electron whose spin is opposite to that of the $2p$ electrons can be excited, so that a net hole is created in the $2s$ shell. Since the $2s$ electron has a much higher charge density at the nitrogen nucleus than do the outer $s$ electrons this excitation is the dominant source of the change in the nitrogen hyperfine splitting. The exchange forces which are of shorter range than the van der Waals forces will have a considerably smaller effect on the inner $2s$ shell of the nitrogen atom. For these reasons we shall consider only the effect of the van der Waals forces on the nitrogen hfs splitting.

Thus, we assume that a nitrogen atom interacting with a matrix particle $M$ is subject to a perturbation $\mathcal{H}'$ where

$$\mathcal{H}' = \mathcal{H}_V + \mathcal{H}_{\text{hfs}}. \tag{1}$$

Here, $\mathcal{H}_V$ is the van der Waals interaction,[9]

$$\mathcal{H}_V = -\frac{e^2}{R^3} \sum_\mu \sum_\nu (2z_{\text{N}\mu} z_{M\nu} - x_{\text{N}\mu} x_{M\nu} - y_{\text{N}\mu} y_{M\nu}), \tag{2}$$

where $R$ is the separation between the interacting particles, $z_{\text{N}\mu}$, $x_{\text{N}\mu}$, and $y_{\text{N}\mu}$ are the coordinates of the $\mu$th electron of the N atom measured from the nitrogen nucleus and $z_{M\nu}$, $x_{M\nu}$, and $y_{M\nu}$ are the coordinates of the $\nu$th electron of the matrix particle measured from the centroid of the charge distribution of $M$. The $z$ coordinates are taken along the axis of the interacting species. The term $\mathcal{H}_{\text{hfs}}$ is the spherically symmetric or contact term in the hyperfine interaction of the nitrogen electrons with the nitrogen nucleus. It is given by the expression of the form[10]

$$\mathcal{H}_{\text{hfs}} = A \sum\nolimits_\mu \delta(\mathbf{r}_{\text{N}\mu}) \mathbf{s}_{\text{N}\mu} \cdot \mathbf{I}_{\text{N}}, \tag{3}$$

where $A$ is a constant which depends on the magnetic moment of the nucleus, $I_{\text{N}}$ is the spin of the nucleus, and $s_{\text{N}\mu}$ is the spin of the $\mu$th nitrogen electron. The dipolar part of the hyperfine interaction will vanish both in a solid where the nitrogen atom is symmetrically surrounded by matrix particles and in a gas where the net effect is the average over collisions having all possible orientations.

For the case of a solid where the N atom interacts with a number of matrix particles it will be assumed that the net change in the hyperfine splitting will be the sum of the shifts produced by the individual matrix particles. This assumption actually requires some explanation since we have earlier assumed that the net effect of the exclusion forces was not simply additive when it was stated that the exclusion forces between an N atom and a symmetric array of matrix particles would distort the nitrogen $p$ orbitals but would not alter their symmetry. Had we treated the hfs shift produced by the exclusion force between the N atom and each matrix particle separately and then added the results a net hfs shift would have resulted. This distinction arises because to a first approximation the exchange forces are regarded as arising from the forbidden overlap of the *averaged charge clouds* of each atom so that the net perturbing force experienced by the N

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[9] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 923.

[10] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

electrons will be the sum of the contributions from the individual matrix particles. This net perturbation will by symmetric for an N atom symmetrically surrounded by matrix particles, and the resultant distortion of the nitrogen $p$ orbitals will not cause them to acquire any $s$ character. The van der Waals forces, on the other hand, are the result of a correlation between the motions of the nitrogen electrons and the electrons of the matrix particles which leads to a force of attraction between the instantaneous dipole moments of the interacting particles. For the case of an N atom interacting with a number of matrix particles, and assuming that the van der Waals interactions between the matrix particles are sufficiently small that there is no correlation between the motion of the electrons on the different matrix particles, then the electrons of each matrix particle can separately correlate their motion with the motions of the electrons of the nitrogen atom so as to maximize the interaction between the instantaneous dipole moment of the N atom and the instantaneous dipole moment of that matrix particle. Under these conditions the van der Waals interaction with each matrix particle is independent of the other matrix particles and the effect of a number of such matrix particles is simply additive. This discussion is only approximate, of course, because the separation of the interaction into an exclusion force between the averaged electron clouds and van der Waals forces due to the correlation between electron motions is somewhat artificial in the region where both effects are important. It is felt, however, that this approximation is satisfactory in a qualitative treatment of the problem.

In order to calculate the shift in the nitrogen hyperfine splitting due to the van der Waals interaction we shall calculate those terms in the energy due to the perturbation $\mathcal{H}'$ which are linear in $\mathcal{H}_{\mathrm{hfs}}$. The first order term is just the hfs splitting of the free N atom. It is readily shown that all second order terms vanish, that is

$$(\mathrm{N}_0M_0|\mathcal{H}_V|\mathrm{N}_iM_j)(\mathrm{N}_iM_j|\mathcal{H}_{\mathrm{hfs}}|\mathrm{N}_0M_0)=0, \tag{4}$$

where $\mathrm{N}_0$ and $\mathrm{N}_i$ are the ground and $i$th excited states of the N atom, and $M_0$ and $M_j$ are corresponding quantities for the matrix particle $M$. Thus, the first contribution to the hfs shift will come from third order terms in the perturbation energy,[8] namely,

$$W_3=\sum_{ij}{}'\sum_{kl}{}'\frac{(00|\mathcal{H}|ij)(ij|\mathcal{H}|kl)(kl|\mathcal{H}|00)}{(E_{00}-E_{ij})(E_{00}-E_{kl})} -(00|\mathcal{H}|00)\sum_{kl}{}'\frac{(00|\mathcal{H}|kl)(kl|\mathcal{H}|00)}{(E_{00}-E_{kl})^2}. \tag{5}$$

Here, the symbol $(ij|\mathcal{H}|kl)$ is an abbreviation for the quantity $(\mathrm{N}_iM_j|\mathcal{H}|\mathrm{N}_kM_l)$. The primes on the summation signs indicate that the ground state $\mathrm{N}_0M_0$ is omitted from the summation.

In order to get the change in the hyperfine splitting energy $\Delta E_{\mathrm{hfs}}$ we select out of $W_3$ those terms which are linear in $\mathcal{H}_{\mathrm{hfs}}$. Omitting vanishing terms such as $(00|\mathcal{H}_V|00)$ gives the relation

$$\Delta E_{\mathrm{hfs}}=2\sum_{ij}{}'\sum_{kl}{}'\frac{(00|\mathcal{H}_V|ij)(ij|\mathcal{H}_V|kl)(kl|\mathcal{H}_{\mathrm{hfs}}|00)}{(E_{00}-E_{ij})(E_{00}-E_{kl})} +\sum_{mn}{}'\sum_{pq}{}'\frac{(00|\mathcal{H}_V|mn)(mn|\mathcal{H}_{\mathrm{hfs}}|pq)(pq|\mathcal{H}_V|00)}{(E_{00}-E_{mn})(E_{00}-E_{pq})} -(00|\mathcal{H}_{\mathrm{hfs}}|00)\sum_{st}{}'\frac{(00|\mathcal{H}_V|st)(st|\mathcal{H}_V|00)}{(E_{00}-E_{st})^2}. \tag{6}$$

It will turn out that the last term in Eq. (6) is considerably smaller than the first two terms and may be neglected. (For a complete discussion of this term, see the Appendix.) Thus, we shall evaluate only the first two terms in Eq. (6).

In the present semiquantitative treatment we shall estimate the sums over the various excited states by the customary process of replacing the energy denominators by appropriate average excitation energies. The choice of the average excitation energies will naturally depend on the nature of the excited states which contribute to the hfs shift so we turn our attention to this question. For the first term in Eq. (6) we note the following:

1. If the matrix element $(kl|\mathcal{H}_{\mathrm{hfs}}|00)$ is to be nonvanishing, then $l$ must be the ground state of the matrix particle, and state $k$ must be either a $(2s)(2p)^3(ns)$ or a $(2s)^2(2p)^2(ns)$ configuration of the nitrogen atom. However, states of the form $(2s)^2(2p)^2(ns)$ cannot be reached in second order from the $(2s)^2(2p)^3$ ground state by the van der Waals perturbation which introduces excited states according to the selection rules

$$\mathcal{H}_V s\rightarrow p \quad\text{and}\quad \mathcal{H}_V p\rightarrow s, \quad\text{or}\quad d.$$

Thus, state $k$ has the configuration $(2s)(2p)^3(ns)$.

2. There will be a net contribution to $\Delta E_{\mathrm{hfs}}$ only if the final state $k$ is reached through an intermediate state $i$ which makes the excitation of the $2s$ electrons spin dependent. This requirement restricts the intermediate state $i$ to be either $(2s)(2p)^4$ or $(2s)^2(2p)^2(ns)$. The intermediate state $(2s)(2p)^4$ requires that the spin of the excited $2s$ electron be opposite to the spins of the $2p$ electrons, while the intermediate state $(2s)^2(2p)^2(ns)$ requires that the subsequent excitation involve that $2s$ electron having the same spin as the $2p$ electrons. Thus, it would appear that the contributions to $\Delta E_{\mathrm{hfs}}$ from these two intermediate states would cancel each other. Closer inspection shows, however, that reversing the order in which the $2s$ and $2p$ electrons are excited to reach the $(2s)(2p)^3(ns)$ final state corresponds to a permutation of the coordinates of the two excited electrons. The permutation of two electrons produces a reversal of sign so that the two intermediate states effectively yield the same final state. The selec-

tion of the average energy for the intermediate states is simplified by the fact that these two states have nearly the same energy.[11] For simplicity we assume that the two excitation energies are equal and have the value denoted by $E_{\mathrm{N}}$.

From these considerations we obtain the following average excitation energies for the first term in Eq. (6):

$$E_{00}-E_{ij}=E_{\mathrm{N}}+E_M, \quad E_{00}-E_{kl}=2E_{\mathrm{N}}. \tag{7}$$

Here, $E_M$ is the average excitation energy of the matrix particle which may be set equal to the ionization energy (with negative sign) for the rare gas atoms. Using the same considerations for the second term in Eq. (6) gives the following estimates of the average excitation energies appropriate to this sum:

$$E_{00}-E_{mm}=E_{00}-E_{pq}=E_{\mathrm{N}}+E_M. \tag{8}$$

By introducing the average excitation energies the first two terms of Eq. (6) may be summed by matrix multiplication. Note that the sum over $k$ in the first term must be completed by the inclusion of the term corresponding to the ground state of the nitrogen atom. This quantity, while not strictly zero is, however, of the same order of magnitude as the third term in Eq. (6) which is shown to be negligible in the Appendix. The result of the summation is

$$\Delta E_{\mathrm{hfs}}=\left[\frac{1}{E_{\mathrm{N}}(E_{\mathrm{N}}+E_M)}+\frac{1}{(E_{\mathrm{N}}+E_M)^2}\right] \times(00|\mathcal{H}_V{}^2\mathcal{H}_{\mathrm{hfs}}|00), \tag{9}$$

where it is to be noted that $\mathcal{H}_{\mathrm{hfs}}$ and $\mathcal{H}_V$ commute.

We introduce Eqs. (2) and (3) for $\mathcal{H}_V$ and $\mathcal{H}_{\mathrm{hfs}}$, respectively, and simplify by noting the following points. Mixed terms such as $z_{M\nu}x_{M\nu'}$ vanish upon integrating over the coordinates of the matrix particle, and for a spherically symmetric matrix particle a term involving the $z$ coordinates of the electrons makes the same contribution as the corresponding terms in the $x$ and $y$ coordinates. This gives the following equation for $\Delta E_{\mathrm{hfs}}$

$$\Delta E_{\mathrm{hfs}}=A\left[\frac{1}{E_{\mathrm{N}}(E_{\mathrm{N}}+E_M)}+\frac{1}{(E_{\mathrm{N}}+E_M)^2}\right]\frac{6e^4}{R^6} \times\sum_{\mu,\mu',\mu''}(0|z_{\mathrm{N}\mu}z_{\mathrm{N}\mu'}\delta(\mathbf{r}_{\mathrm{N}\mu''})\mathbf{S}_{\mathrm{N}\mu''}\cdot\mathbf{I}_{\mathrm{N}}|0) \times\sum_{\nu,\nu'}(0|z_{M\nu}z_{M\nu'}|0). \tag{10}$$

In the present treatment it is not only likely to be more accurate, but is inherently desirable to relate as many of the theoretical terms as possible to experimental quantities. Thus, we introduce the polarizability of the matrix particle $\alpha_M$ which is given by the expression[12]

$$\alpha_M=-\frac{2e^2}{E_M}\sum_{\nu,\nu'}(0|z_{M\nu}z_{M\nu'}|0). \tag{11}$$

This leads to the relation

$$\Delta E_{\mathrm{hfs}}=-A\frac{3e^2}{R^6}\left(\frac{1}{E_{\mathrm{N}}}+\frac{1}{E_{\mathrm{N}}+E_M}\right)\frac{E_M\alpha_M}{E_{\mathrm{N}}+E_M} \times\sum_{\mu,\mu',\mu''}(0|z_{\mathrm{N}\mu}z_{\mathrm{N}\mu'}\delta(\mathbf{r}_{\mathrm{N}\mu''})\mathbf{S}_{\mathrm{N}\mu''}\cdot\mathbf{I}_{\mathrm{N}}|0). \tag{12}$$

The simplest way to evaluate this last expression is to consider the ESR experiment where the electron and nuclear spins are quantized independently along an external magnetic field, and to evaluate the matrix element for the state where $M_S=S=\frac{3}{2}$.[13] For this case the ground-state wave function is

$$\psi_0=(5!)^{-\frac{1}{2}}\det|s_\alpha(1)s_\beta(2)x_\alpha(3)y_\alpha(4)z_\alpha(5)|, \tag{13}$$

where $s$ is the nitrogen $2s$ orbital, $x$, $y$, and $z$ denote the nitrogen $2p$ orbitals oriented along the indicated directions, and $\alpha$ and $\beta$ denote the parallel and antiparallel electron spin orientations. In evaluating the matrix element with the above wave function it may be noted that the determinantal form is essential because the only nonvanishing terms involve exchange of the $s_\alpha$ and $z_\alpha$ orbitals. This is to be expected from the earlier discussion which showed that the action of the van der Waals forces in influencing the hyperfine splitting involved excitation of the $2s$ electrons into the $2p$ shell, a process which was spin dependent because the $2p$ shell was half filled. Upon computing this matrix element and noting that in a strong magnetic field the hyperfine splitting energy is given by the expression

$$E_{\mathrm{hfs}}=A_{\mathrm{N}}M_SM_I, \tag{14}$$

one gets the following expression for the change in the hfs splitting constant of $\mathrm{N}^{14}$:

$$\Delta A_{\mathrm{N}^{14}}=-\frac{2e^2}{R^6}\left(\frac{1}{E_{\mathrm{N}}}+\frac{1}{E_{\mathrm{N}}+E_M}\right)\frac{E_M\alpha_M}{E_{\mathrm{N}}+E_M} \times(s|z|z)^2A_{\mathrm{N}^{14}2s}. \tag{15}$$

Here $A_{\mathrm{N}^{14}2s}$ is the hyperfine splitting constant for a $2s$ electron of $\mathrm{N}^{14}$, and $(s|z|z)$ is the matrix element of the operator $z$ evaluated between the nitrogen $2s$ and $2pz$ orbitals.

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[11] R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932), p. 293.

[12] H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944), p. 121.

[13] The shift in the hyperfine splitting constant will naturally be the same with or without an applied magnetic field. The hyperfine splitting can be calculated for the case of zero magnetic field using the usual methods of the theory of angular momentum operators. See, for example, E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1951), Chap. 3.

The following values will be used for the nitrogen atom parameters appearing in Eq. (15). Using the Hartree atomic orbitals of nitrogen[14] it was found that $(s|z|z)^2=0.607a_0^2$ and $A_{\mathrm{N}^{14}2s}=1510$ Mc/sec. The average excitation energy of the nitrogen atom $E_{\mathrm{N}}$ was taken to be the energy required to excite a $2s$ electron into the $2p$ shell. This gave $E_{\mathrm{N}}=-0.402e^2/a_0$.[11]

## RESULTS AND DISCUSSION

### N Atoms in a Solid Matrix

We shall use the present theory along with the experimental results for the shift in the nitrogen hyperfine splitting to estimate the separation of the trapped N atom from the nearest neighbor matrix atoms. This value can be compared with the value predicted from the crystal structure of the host matrix for different possible sites which the trapped atom may occupy.

The inert gases neon, argon, etc. crystallize in a face-centered cubic structure.[15] At liquid helium temperature nitrogen also crystallizes in a face-centered cubic structure.[16] In a face-centered cubic lattice there are three possible trapping sites: (1) substitutional site; (2) octahedral site, and (3) tetrahedral site.[5] The number of nearest neighbor matrix atoms for the substitutional, octahedral, and tetrahedral sites are 12, 6, and 4, respectively.

In Table I we have calculated for each type of site the nearest-neighbor distance $R_{\mathrm{cal}}$ which when used in Eq. (15) gives the observed shift in the nitrogen hyperfine splitting. This value is compared with the observed nearest-neighbor distance for the various possible sites in the perfect crystal. From these results it is clear that the best agreement between the calculated and observed separations is obtained when the N atom is trapped substitutionally, and that a nitrogen atom trapped in either of the interstitial sites would experience a much larger hfs shift than is observed unless there was a marked outward distortion of the lattice. Thus, it is very likely that the nitrogen atoms are trapped substitutionally in these matrices. This conclusion is in agreement with the results obtained for hydrogen atoms in these matrices, which indicated that when the hydrogen atoms were produced in the gas phase by electric discharge and frozen out along with the matrix gas that all the hydrogen atoms entered the matrix substitutionally. Only when the hydrogen atoms were produced in the matrix at 4.2°K by the photolytic dissociation of HI did one get additional ESR lines which were interpreted as due to interstitially trapped H atoms.[5] Since all the nitrogen atom results are based on deposition from the gas phase, it is very unlikely that any of the nitrogen atoms would enter interstitial sites if the smaller hydrogen atoms were unable to do so.

TABLE I. Comparison of the nearest-neighbor distance ($R_{\mathrm{cal}}$) required to give the observed shift in the nitrogen hyperfine splitting with the corresponding distance ($R_{\mathrm{obs}}$) in the perfect crystal. The calculation is made for nitrogen atoms trapped in the substitutional site and two interstitial sites of the host crystal.

| Matrix | $\Delta A_{\mathrm{N}^{14}}$ (Mc/sec) | Site | $R_{\mathrm{cal}}$ ($a_0$) | $R_{\mathrm{obs}}$ ($a_0$) |
|---|---|---|---|---|
| Ne | 1.00[2] | Subs. | 7.08 | 5.81[15] |
| | | Oct. | 6.31 | 4.11 |
| | | Tet. | 5.90 | 3.56 |
| Ar | 2.15[2] | Subs. | 7.84 | 7.09[15] |
| | | Oct. | 6.98 | 5.01 |
| | | Tet. | 6.53 | 4.34 |
| $N_2$ | 1.63[1] | Subs. | 8.32 | 7.57[16] |
| | | Oct. | 7.41 | 5.36 |
| | | Tet. | 6.93 | 4.63 |

### Nitrogen Atoms in Buffer Gases

A nitrogen atom in the presence of a buffer gas will experience collisions with the buffer gas particles which will change the nitrogen hfs constant. Unless the buffer gas pressure is extremely low the net shift will be the average over all types of collisions. This average over collisions which is essentially a time average may, according to the usual procedures of statistical mechanics, be replaced by an ensemble average which gives us the following equation for the average hfs shift $\langle\Delta A_{\mathrm{N}}\rangle$:

$$\langle\Delta A_{\mathrm{N}}\rangle=\rho\int\Delta A_{\mathrm{N}}(R)\exp[-U(R)/kT]d\tau. \qquad (16)$$

Here, $U(R)$ is the interaction energy between a nitrogen atom and a buffer gas particle and $\rho$ is the density of buffer gas particles.

In order to estimate the integral in Eq. (16), we represent $U(R)$ by a Lennard-Jones 6–12 potential,[17]

$$U(R)=4\epsilon[(\sigma/R)^{12}-(\sigma/R)^6]. \qquad (17)$$

The parameter $\sigma$ is a measure of the collision diameter of the interacting particles and $\epsilon$ is the maximum energy of attraction or depth of the potential well. The collision diameter $\sigma$ is the sum of the collision radii of the interacting particles, that is

$$\sigma=\tfrac{1}{2}\sigma_{\mathrm{N}}+\tfrac{1}{2}\sigma_M. \qquad (18)$$

The collision radii of the buffer gases are known from such properties as their virial coefficients[18] and $\frac{1}{2}\sigma_{\mathrm{N}}$ will be estimated from an empirical rule due to Pauling[19]:

$$\tfrac{1}{2}\sigma_{\mathrm{N}}=R\text{ (covalent single bond)}+1.5a_0\cong2.9a_0.$$

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[14] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A193**, 299 (1948).

[15] E. R. Dobbs and G. O. Jones, *Reports on Progress in Physics* (The Physical Society, London, 1957), Vol. 20, p. 560.

[16] M. Ruhemann, Z. Physik **76**, 368 (1932).

[17] Reference 9, p. 32.

[18] Reference 9, pp. 162 and 1110.

[19] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), 3rd ed., p. 263.

TABLE II. The maximum energy of attraction $\epsilon$ between a nitrogen atom and various buffer gas molecules.

| Gas | $\sigma$ ($a_0$) | $E_V$ ($e^2/a_0$) | $\epsilon/k$ (deg K) |
|---|---|---|---|
| He | 5.35 | $-7.93/R^6$ | 26.7 |
| Ne | 5.51 | $-14.6/R^6$ | 41.2 |
| Ar | 6.12 | $-54.8/R^6$ | 82.3 |
| $N_2$ | 6.41 | $-59.5/R^6$ | 67.7 |

Our estimate of $\epsilon$ is very rough and is obtained by computing the van der Waals interaction energy $E_V$ as described in the Appendix and using the relation

$$E_V=-4\epsilon(\sigma/R)^6. \quad (19)$$

Fortunately it will turn out that the results are only slightly dependent on the value of $\epsilon$. Using the formula for $E_V$ given in the Appendix the values of $\epsilon$ were computed for the various buffer gases. These results are given in Table II.

Using Eq. (15) for $A_N$ and Eq. (17) for $U(R)$ in Eq. (16) gives

$$\langle\Delta A_N\rangle=\frac{4\pi\rho C_M}{\sigma^3}\int_0^\infty r^{-4}\exp\left[-\frac{4}{T^*}\left(\frac{1}{r^{12}}-\frac{1}{r^6}\right)\right]dr. \quad (20)$$

Here, $\Delta A_N(R)$ has been written as $C_M/R^6$ where $C_M$ is a constant depending only on the matrix gas, $r=R/\sigma$ and $T^*=kT/\epsilon$. The integral in Eq. (20) which we denote as $I(T^*)$ can be evaluated for the values of $T^*$ encountered here by a method described by Hirschfelder *et al.*[20] This method expands the exponential term in $r^{-6}$ in a power series to obtain a series expansion for $I(T^*)$. The results of this integration are given in Fig. 1. For a bulb temperature of 343°K and the values of $\epsilon/k$ given in Table II the function $I(T^*)$ varies only from 0.50 to 0.46 in going from helium to argon. Thus, the results will be quite insensitive to the exact value chosen for $\epsilon$. It also follows that the hfs shift will be very insensitive to fluctuations in temperature.

The results for the pressure shifts in various buffer gases are given in Table III. Comparison with the experimental values shows that the calculated results are of the right order of magnitude, but are consistently too high by a factor of 2 to 3. The calculation contains several approximations which may contribute to the discrepancy between theory and experiment. For one thing the average excitation energy of the nitrogen atom $E_N$ was chosen to correspond to one of the lowest excited states, namely the $(2s)(2p)^4$ state, because of the key role that this state played in producing spin unpairing in the $2s$ shell. However, higher excited states are also present in the excited wave function and a detailed analysis of their contribution would probably result in the choice of a larger value for $E_N$. This would reduce the calculated value of the nitrogen hyperfine splitting. Another factor is the use of Hartree-Fock wave functions for the ground state of the nitrogen atom. Since the Hartree-Fock method neglects correlation between the electrons, except for correlation due to the exclusion principle, it tends to give wave functions which are somewhat too diffuse. As a result matrix elements such as $(s|z|z)$ which appears in Eq. (15) may be somewhat too large. This also would overestimate the shift in the nitrogen hyperfine splitting.

TABLE III. Effect of various buffer gases on the nitrogen hyperfine splitting constant. Results are in cycles/sec mm Hg for a bulb filled at room temperature.

| Gas | $\langle\Delta A_{N^{14}}\rangle_{\text{theory}}$ | $\langle\Delta A_{N^{14}}\rangle_{\text{exp}}$[a] |
|---|---|---|
| He | 1.1 | 0.32 |
| Ne | 1.8 | 0.57 |
| Ar | 5.0 | 1.93 |
| $N_2$ | 4.8 | 2.40 |

[a] See reference 4.

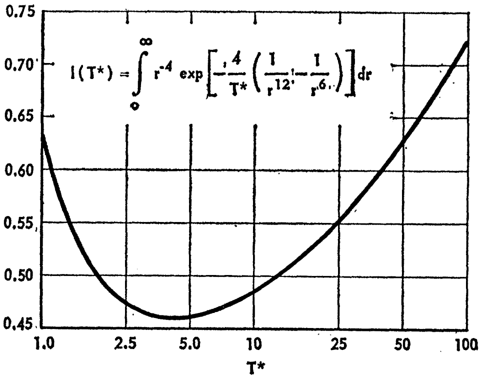

FIG. 1. Integral giving the dependence of the shift in the nitrogen hyperfine splitting constant on temperature and on the maximum energy of attraction ($\epsilon$) between the nitrogen atom and the buffer gas particle. Here $T^*=kT/\epsilon$, and for convenience a logarithmic scale is used for the abscissa.

The results for nitrogen atoms in solid matrices also suggest that the computed results are high by a factor of two since the computed nearest-neighbor distances are somewhat greater than the nearest neighbor distances in the host crystal. Reduction of the computed hyperfine splitting shift by a factor of two would reduce the calculated nearest neighbor distance in Table I by a factor of $(2)^{1/6}$, and they would then be in close agreement with the nearest neighbor distances $R_{\text{obs}}$ of the perfect crystals. Thus, the present theory gives good correlation between the results obtained for nitrogen atoms trapped in solids and in buffer gases.

## CONCLUSIONS

It appears that the shift in the nitrogen hyperfine splitting produced by the interaction of the nitrogen atom with a host matrix or a buffer gas is largely the result of van der Waals interactions. The effect of the

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[20] Reference 9, p. 163.

van der Waals forces is chiefly to introduce $(2s)(2p)^4$ excited states into the nitrogen wave function. Since the $2p$ shell of the $^4S$ nitrogen atom already contains three electrons of the same spin only that $2s$ electron with the opposite spin can be excited. This creates a positive spin density at the nucleus, which increases the already positive free-atom hyperfine splitting constant. The magnitude of the effect depends linearly on the polarizability of the perturbing species so that the shift tends to increase as one goes to larger more polarizable atoms and molecules.

A similar but larger effect could be produced by the electric field of a polar molecule. Moreover, this mechanism can produce changes in the hyperfine splitting constants of nitrogen nuclei in $\pi$-electron free radicals just as it did for the free nitrogen atom. Thus, one might expect relatively large variations in the hfs splitting constants of nitrogen nuclei for free radicals in highly polarizable or polar solvents.

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## APPENDIX

In this section we shall estimate the van der Waals interaction energy between a nitrogen atom and a matrix particle, and incidentally obtain an estimate of the third term in Eq. (6) which was claimed to be negligible.

Second-order perturbation theory gives the following formula for the van der Waals energy

$$E_V=\frac{e^4}{R^6}\sum_{i,j}{}' \sum_{\mu,\mu'}\sum_{\nu,\nu'}(E_{00}-E_{ij})^{-1} \times(00|2z_{\mathrm{N}\mu}z_{M\nu}-x_{\mathrm{N}\mu}x_{M\nu}-y_{\mathrm{N}\mu}y_{M\nu}|ij) \times(ij|2z_{\mathrm{N}\mu'}z_{M\nu'}-x_{\mathrm{N}\mu'}x_{M\nu'}-y_{\mathrm{N}\mu'}y_{M\nu'}|00), \qquad \text{(A1)}$$

where we have used Eq. (2) for the van der Waals Hamiltonian. Now a given excited state $(ij)$ can be reached by only one of the operators $z_{\mathrm{N}\mu}z_{M\nu}$, $x_{\mathrm{N}\mu}x_{M\nu}$ or $y_{\mathrm{N}\mu}y_{M\nu}$. If the matrix particle is spherically symmetric, then all three operators will be equally effective so that

$$E_V=\frac{6e^4}{R^6}\sum_{i,j}{}' \sum_{\mu,\mu'}\sum_{\nu,\nu'}\frac{(00|z_{\mathrm{N}\mu}z_{M\nu}|ij)(ij|z_{\mathrm{N}\mu'}z_{M\nu'}|00)}{(E_0-E_i)+(E_0-E_j)} \qquad \text{(A2)}$$

If we replace the energy denominators by average energies for the excited states of the nitrogen atom $(E_{\mathrm{N}})$ and the matrix particle $(E_M)$, use Eq. (11) for the polarizability of the matrix particle, and sum over the excited states of the nitrogen atom by matrix multiplication, we obtain the result

$$E_V=\frac{-3e^2}{R^6}\frac{\alpha_M E_M}{E_{\mathrm{N}}+E_M}\sum_{\mu\mu'}(0|z_{\mathrm{N}\mu}z_{\mathrm{N}\mu'}|0). \qquad \text{(A3)}$$

Using the Hartree orbitals of nitrogen[14] and the wave function of Eq. (13) it was found that $\sum_{\mu,\mu'}(0|z_{\mathrm{N}\mu}z_{\mathrm{N}\mu'}|0)=2.792$, so that

$$E_V=\frac{-8.38e^2}{R^6}\frac{\alpha_M E_M}{E_{\mathrm{N}}+E_M}. \qquad \text{(A4)}$$

Here $E_{\mathrm{N}}$ was assigned the value $-0.40e^2/a_0$ and $E_M$ was taken to be the ionization energy (with negative sign) of the matrix particle. The van der Waals interaction energies of the nitrogen atom with various matrix particles are given in Table II.

We can now estimate the third term in Eq. (6) by using the average energy approximation for the energy denominator. This term is of the order of magnitude $A_{\mathrm{N}}E_V/(E_{\mathrm{N}}+E_M)$, where $A_{\mathrm{N}}=10.45$ Mc/sec is the hfs splitting of the free nitrogen atom.[3] In argon, $E_{\mathrm{N}}+E_M=-0.98e^2/a_0$ and $E_V=-54.8/R^6$, so that the contribution of this term to the hfs shift is $584/R^6$. This is negligible in comparison to the contribution of the first two terms in Eq. (6) which produce a hfs shift of $42\,100/R^6$.