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PHYSICAL REVIEW A VOLUME 7, NUMBER 2 FEBRUARY 1973

Structure of the Adsorbed Helium Film near Monolayer Densities*

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A variational wave function is constructed for the ground state of He^3 and He^4 films adsorbed on graphite when the density is near that of a completed monolayer. By using this wave function, the density of the completed monolayer is calculated while the exchange effects and Debye temperatures are estimated. Comparisons with experiments are made. The pair-distribution function and the corresponding structure factor and Debye–Waller parameter are predicted.

I. INTRODUCTION

The general view of the adsorbed helium film is that near monolayer densities, the film exists as a compressed two-dimensional solid.[1] For instance, assuming two-dimensional close packing for He^4 adsorbed on graphite, the measured areal density of 0.115 Å^{-2} for the monolayer[2] corresponds to a nearest-neighbor distance of 3.17 Å, much less than the 3.68-Å nearest-neighbor distance for the three-dimensional solid at 0 K and 25 atm. In fact, it is necessary to pressurize the solid at almost 500 atm to attain nearest-neighbor distances less than 3.2 Å. Debye-temperature measurements of the film[2] are consistent with this conception of the monolayer. Measured Debye temperatures of the film correspond to those of the solid pressurized from 300 to 500 atm. The cause of this compressional phenomena is the strong attractive interaction between the helium atoms and the graphite substrate. The energy it costs to compress the film by adding additional adatoms is compensated by the energy which is gained by having more adatoms in the deep potential well near the graphite surface. The monolayer density is then determined by a simple energy-balance criterion.[3]

Thermodynamic measurements cannot unambiguously determine the structure or phase of the monolayer. A definitive measurement could, however, be provided by a neutron scattering experiment. Such an experiment is now in the planning stages.[4] This type of experiment can measure the structure factor $S(Q)$ which is the Fourier transform of the pair-distribution function $g(r)$.[5] The calculation of $g(r)$, which is obtainable from the ground-state wave function, is the main motivation for this work.

The history of theoretical investigations of solid helium has demonstrated that short-range correlations, of the type incorporated into Jastrow wave functions, can be very important.[6] It would be expected then that these same correlations are also important in the adsorbed film. This expectation has, in fact, been demonstrated as correct at densities around 25 to 50% that of the monolayer, where there exists a liquid ground state.[7] However, recent theoretical investigations of quantum solids under very high pressure (greater than 10^3 bar) conclude that under these conditions two-particle correlations are not important and that quantum solids become harmonic solids.[8] Thus, it seems reasonable to expect the Gaussian–Hartree approximation[9] to be valid if applied to the ground state of the adsorbed helium film near monolayer densities.

The helium monolayer is assumed to be a close-packed two-dimensional solid, and a variational wave function is constructed as a product of Gaussians, each Gaussian centered on a lattice site. The width of the Gaussians is the variational parameter. The helium-helium interaction is described by semiempirical Morse V_{DD} two-body potential.[10] The density of monolayer completion at 0 K is calculated for both He^3 and He^4 by comparing the chemical potential of the film to the energy of adsorption of a single helium atom upon the first layer. The calculated monolayer densities are in excellent agreement with experiment. The magnitude of exchange effects in the film and the behavior of the Debye temperature with density are estimated and compared to experiment. Finally, the pair-distribution function, Debye–Waller factor, and structure factor are predicted.

II. VARIATIONAL CALCULATION

The adsorbed film on an arbitrary substrate is only approximately a two-dimensional system with the adatom wave function being only approximately separable in the coordinate perpendicular to the surface. The reason for this is twofold. Not only is the adatom-substrate potential not separable, but the adatom-adatom potential is not simply a function of the lateral separation of the adatoms due to their zero-point oscillations perpendicular to the surface. However, calculated quantum states for helium adsorbed on graphite have a nearly separable nature for energies less than 80 K above the ground state.[11] These states are essentially separable in the perpendicular coordinate with a functional dependence on this coordinate which is independent of the particular state. Furthermore, the adatom wave function is sharply peaked at about 3.2 Å away from the graphite surface with a rms displacement of about 0.3 Å. An appropriate effective lateral potential which accounts for adatom motion perpendicular to the surface can be written for two adatoms separated by a distance r along the surface.[3] However, because of the sharpness of the wave function perpendicular to the plane, this effective potential differs little from that obtained by localizing the adatoms in the same plane. For example, motion perpendicular to the plane causes the position of the potential zero, the position of the potential minimum, and the minimum value of the potential to all change by about 1%. Thus, the major effect of the graphite substrate is to confine the helium atoms to motion in two dimensions having little effect upon the helium-helium interaction but causing the lowest single-particle energy to be below the vacuum zero by just the energy of adsorption.[11]

Taking the energy origin at the single-particle ground-state energy, the film is described by the two-dimensional Hamiltonian

$$\hat{H}=\sum_{j=1}^{N} -\frac{\hbar^2}{2M}\nabla_j^2+\frac{1}{2}\sum_{ij} V(\vec{r}_i-\vec{r}_j)\ , \tag{1}$$

where M is the adatom mass, N is the number of adatoms, $V(r)$ is the helium-helium potential, and $\vec{r}_j$ is the position vector of the jth adatom. The form used for $V(r)$ is the semiempirical Morse V_{DD} potential[10]:

$$V(r)=\epsilon\left[e^{-2c(1-r/r_M)}-2e^{-c(1-r/r_M)}\right]\ , \quad r< r_1 \tag{2a}$$

$$V(r)=-C_6r^{-6}-C_8r^{-8}\ , \qquad r\geq r_1 \tag{2b}$$

with C_6 and C_8 being the theoretical dipole-dipole and dipole-quadrupole interactions and ϵ, c, r_M, and r_1 chosen so that $V(r)$ and its first derivative are continuous and so that $V(r)$ fits the virial coefficient data. This form for $V(r)$ can be compared to the *ab initio* calculations of the helium-helium potential.[12] Figure 1 shows $V(r)$ plotted together with the calculated points of Schaefer *et al.* near the potential minimum and the slightly less accurate points of Bertoncini and Wahl away from the minimum. The agreement is excellent.

A variational ground-state wave function is constructed as a product of Gaussians, each Gaussian centered on a lattice site of the simple hexagonal lattice. The overlap is assumed entirely negligible, an assumption which will be justified *a poste-*

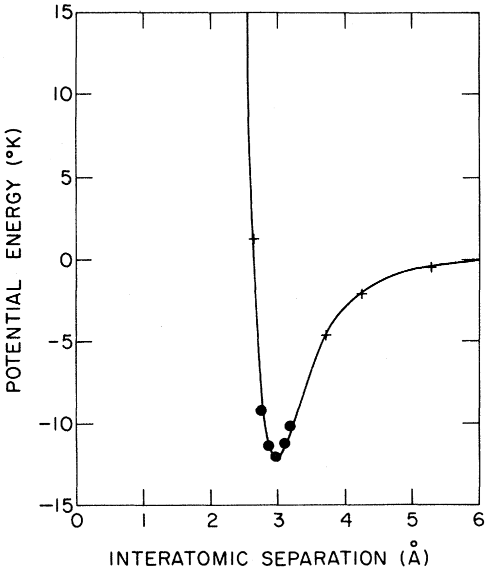

FIG. 1. Helium-helium interatomic potential. The solid line is the Morse V_{DD} potential (Ref. 10), the solid circles are the calculated values of Schaefer *et al.* (Ref. 12), and the crosses are the calculated values of Bertoncini and Wahl (Ref. 12).

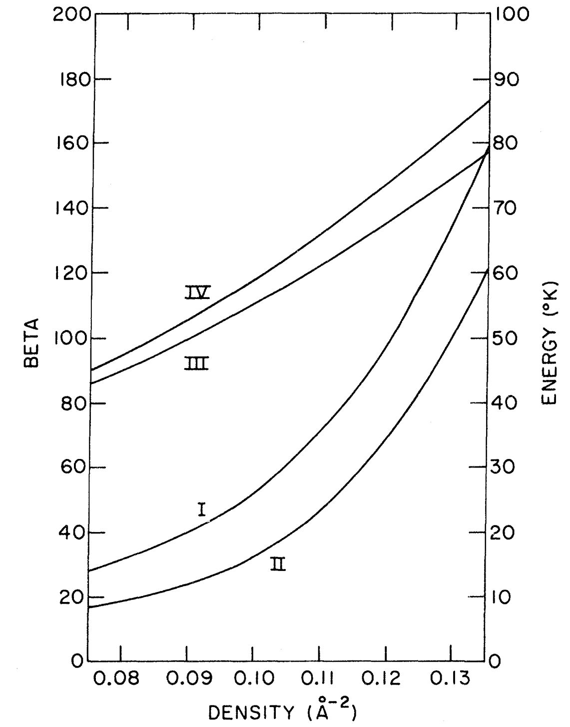

FIG. 2. Calculated ground-state parameters for the helium film as a function of the areal density ρ. Curve I is the energy per atom $\epsilon(\rho)$ for He^3; curve II is $\epsilon(\rho)$ for He^4; curve III is the variational parameter $\beta(\rho)$ for He^3; and curve IV is $\beta(\rho)$ for He^4.

riori. The localization this implies makes it unnecessary to symmetrize or antisymmetrize the wave function; hence, the same form is used for both He^3 and He^4. The trial wave function is

$$\Psi(\vec{r}_1, \ldots, \vec{r}_N) = \left[\frac{\alpha}{2\pi}\right]^{N/2} \prod_{j=1}^{N} e^{-\alpha(\vec{r}_j - \vec{R}_j)^2/4} , \tag{3}$$

where $\vec{r}_j$ is the position vector of the jth adatom, $\vec{R}_j$ is the lattice vector for the jth lattice site, and α is a variational parameter determined by minimizing the total energy at constant density ρ. The density is related to a, the lattice constant or nearest-neighbor distance, via

$$\rho = 2/a^2\sqrt{3} \ . \tag{4}$$

The kinetic energy can be evaluated immediately with

$$\frac{T}{N} = \frac{\hbar^2}{2M} \sum_{j=1}^{N} \frac{1}{N} \langle \Psi | \nabla_j^2 | \Psi \rangle = \frac{\hbar^2 \alpha}{4M} \ . \tag{5}$$

The potential energy has a simple form with

$$U = \frac{1}{2} \sum_{ij} \langle \Psi | V_{ij} | \Psi \rangle$$

$$= \left(\frac{\alpha}{2\pi}\right)^2 \int dr_{j_1}{}^2 dr_{j_2}{}^2 \, V(\vec{r}_{j_1} - \vec{r}_{j_2})$$

$$\times e^{-\alpha[(\vec{r}_{j_1} - \vec{R}_{j_1})^2 + (\vec{r}_{j_2} - \vec{R}_{j_2})^2/2} \ . \tag{6}$$

Doing the $\vec{r}_{j_1} + \vec{r}_{j_2}$ integration in center-of-mass coordinates,

$$\frac{U}{N} = \frac{\alpha}{4} \sum_j \nu_j \int_0^\infty dr\, r\, V(r) e^{-\alpha(r-\Delta_j)^2/4} e^{-z} I_0(z) ,$$

$$z = \tfrac{1}{2} \alpha r \Delta_j , \tag{7}$$

where $I_0(z)$ is the modified Bessel function of order zero and is given by

$$I_0(z) = \frac{1}{\pi} \int_{-1}^{1} dy \, [e^{zy}/(1-y^2)^{1/2}] \ . \tag{8}$$

The summation is over nearest-neighbor shells with ν_j and Δ_j being, respectively, the number of atoms in and the radius of the jth shell. The energy per atom is then $\epsilon = (T + U)/N$.

The parameter α is determined numerically as a function of ρ. Figure 2 is a plot of $\beta = a^2\alpha$ and of ϵ as functions of ρ. The positive values of ϵ are indicative of the film being under compression at these densities. The large values of β mean that the helium atom is effectively localized about a lattice site. The rms distance from the lattice site is $a(2/\beta)^{1/2}$ and β varies from about 90 to 170. The overlap is negligible since it is given by $e^{-\alpha(\vec{R}_j - \vec{R}_i)^2/4}$. For R_j and R_i nearest neighbors, this factor varies from 10^{-10} to 10^{-20}. Furthermore, the probability of two adatoms being found at a separation less than the hard-core separation is small. In a situation of this kind, Jastrow-type correlations can be expected to have only minor effects.[6] The localization rules out any measurable exchange effects (and consequently, any spin ordering in the He^3 films) due to the exchange integral being dominated by the overlap factor. This is consistent with experiments which show that any evidence of spin ordering disappears at densities well below that of the monolayer.[13]

The chemical potential μ_1 of the monolayer is obtained by numerical differentiation of $\epsilon(\rho)$ using

$$\mu_1 = \epsilon(\rho) + \rho \frac{d\epsilon(\rho)}{d\rho} \ . \tag{9}$$

The monolayer completes when μ_1 is equal to μ_2, the chemical potential of a single atom adsorbed upon the first layer. The value of μ_2 is taken directly from Ref. 3 where the method of calculation is discussed. Although the helium-helium interaction used in Ref. 3 is different from that used here, the small difference in final values of μ_2 would have little effect upon the calculated monolayer density because μ_1 is such a steep function of ρ. Figure 3 shows μ_1 and μ_2 plotted as functions of ρ for both He^3 and He^4. The calculated densities for monolayer completion at 0 K are 0.110 $\mathring{A}^{-2}$ for He^3 and 0.116 $\mathring{A}^{-2}$ for He^4. These are in excellent agree-

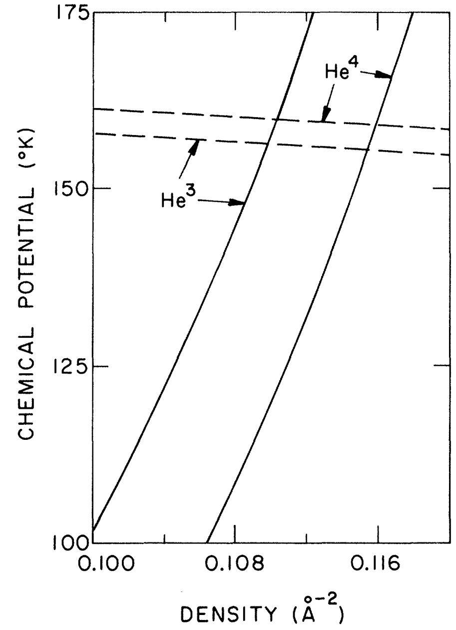

FIG. 3. Chemical potentials μ_1 (solid lines) and μ_2 (dashed lines) for both isotopes.

ment with the experimental[2,14] values of 0.107 Å^{-2} for He^3 and 0.115 Å^{-2} for He^4, especially since the experimental results are finite temperature values and the monolayer density should increase slightly as the temperature is lowered.

In the limit of very high pressure, the calculation of the Debye temperature is straightforward. In this limit, the film is a harmonic solid with extremely localized atoms. The zero-point energy is then just the kinetic zero-point energy, and this can be set equal to the zero-point energy of the Debye phonons. In two dimensions, the Debye phonon zero-point energy is

$$E_0 = \tfrac{2}{3} Nk\Theta_D \ . \tag{10}$$

Equating this to the zero-point kinetic energy, the Debye temperature is given by

$$\Theta_D = \sqrt{\tfrac{27}{16}}\ (\hbar^2 \rho\beta/Mk) \ . \tag{11}$$

For densities below or at monolayer density, Eq. (11) can be expected to give only an estimate of Θ_D. However, this equation should give the asymptotic behavior and agreement with experiment should improve as the density approaches that of the monolayer. Figure 4 is a plot of Eq. (11) as a function of ρ for He^4. The experimental values are also plotted. Agreement between the calculated and measured Debye temperatures is satisfactory at the monolayer density but less so at the lower portion of the density range. However, there is a definite asymptotic relationship between the data and Eq. (11).

III. STRUCTURE FACTOR

The elastic coherent neutron scattering from a solid exhibits sharp peaks in momentum space owing to Bragg scattering.[5] For a two-dimensional solid, these peaks occur along lines perpendicular to the plane. For momentum transfers in the plane, these peaks occur at momentum transfers Q equal to 2π times the reciprocal lattice vectors; with the height of a peak proportional to the Debye–Waller factor e^{-2w}, where

$$e^{-W} = \langle \Psi | e^{i\vec{Q}\cdot(\vec{r}_j - \vec{R}_j)} | \Psi \rangle \ . \tag{12}$$

Using Eq. (3), the Debye–Waller parameter w can be easily evaluated with

$$w = a^2 Q^2 / 2\beta \ . \tag{13}$$

Thus the Bragg scattering gives an experimental measurement of the structure and the degree of localization of the two-dimensional solid.

Neutron scattering can also be used to experimentally determine $S(Q)$, the Fourier transform of the pair-distribution function $g(r)$.[5] The two-dimensional structure factor is given by

$$S(Q) = 1 + 2\pi\rho \int_0^\infty dr\, r[g(r) - 1] J_0(Qr) \ , \tag{14}$$

where Q is the magnitude of the momentum transfer (assumed to be parallel to the plane), $J_0(z)$ is the Bessel function of order zero, and $2\pi r\rho g(r)\, dr$ is equal to the number of atoms in a ring of radius r and width dr about a given atom. The measurement of $S(Q)$ involves both elastic and inelastic coherent scattering, but the rms energy spread is

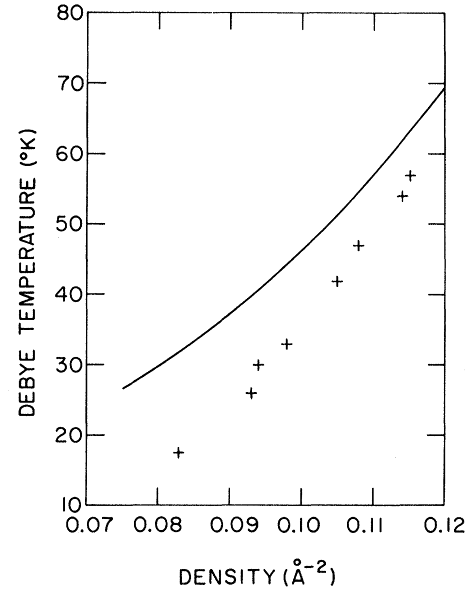

FIG. 4. Debye temperatures for the He^4 film. The solid line is calculated using Eq. (11); the crosses are the experimental values of Bretz and Dash (Ref. 2).

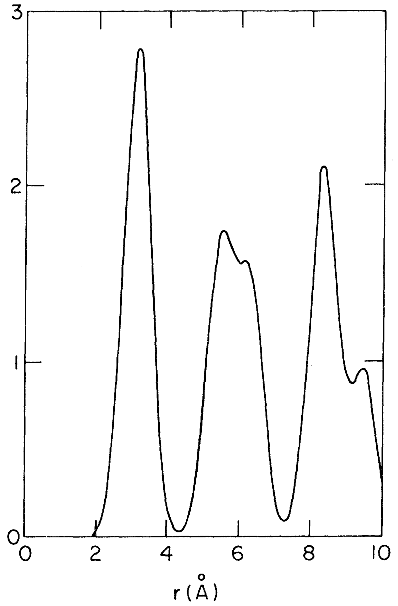

FIG. 5. Pair-distribution function $g(r)$ calculated for He^4 with $\rho = 0.116$ Å^{-2}.

related in a simple manner to $S(Q)$ via[5]

$$\Delta E_{\mathrm{rms}} = [\hbar^2 Q^2 kT / M S(Q)]^{1/2} , \tag{15}$$

where M is the neutron mass, k is the Boltzmann constant, and T the absolute temperature.

The pair distribution function for He^4 at $\rho = 0.116$ Å^{-2} is plotted in Fig. 5. There are sharp peaks in $g(r)$ at the locations of the various nearest-neighbor shells and sharp dips between shells. The behavior of $g(r)$ shows the oscillations characteristic of long-range order. These oscillations produce sharp peaks in $S(Q)$ reflecting the Bragg scattering of such an ordered system. These peaks would be broadened, however, by any disorder in the monolayer.

The graphite surface is not a flat surface even though it is a very smooth one. Furthermore, the periodic structure of the substrate is not commensurate with the periodic structure of the monolayer, and thus, could be expected to slightly disorder the monolayer. The effects of disorder can be phenomenologically incorporated by modifying $g(r)$ so that the long-range oscillations are damped. The modified $g(r)$ can then be used to calculate a model $S(Q)$. A modified $g(r)$ can be defined by

$$\tilde{g}(r) = 1 + (1/\eta)[g(r) - 1] e^{-\gamma r} , \tag{16}$$

where γ is a parameter indicating the amount of disorder and η is a normalization constant adjusted so that $S(Q = 0) = 0$. It is possible to find at least one value of γ such that η is unity. Under these conditions there is no modification of $g(r)$ for small r, but $\tilde{g}(r)$ has only damped oscillations and goes to unity at large values of r. By using $\tilde{g}(r)$ in Eq. (14) instead of $g(r)$, the integration can be truncated at some large value of r without introducing spurious oscillations into $S(Q)$. Furthermore, $S(Q)$ now has peaks of finite height and width. Figure 6 is a plot of $S(Q)$, calculated with $\gamma = 0.09175$ Å^{-1} for He^4 at a density of 0.116 Å^{-2}. With this value of γ, $\eta = 1$. The oscillations in $\tilde{g}(r)$ have essentially disappeared beyond $r = 20$ Å, that is, beyond the 17-nearest-neighbor shell. Although this corresponds to a reasonable amount of disorder, the Bragg peaks are still fairly sharp. The decrease in the heights of the peaks with increasing Q is given roughly by the Debye-Waller factor. Using Eq. (15), the rms energy spread for the first Bragg peak with $T = 1.0$ K is about 3 K. The energy spread associated with the other peaks is somewhat larger. With thermal neutrons, such an energy spread has a corresponding momentum spread which is about 1% of the Q value associated with the first Bragg peak. Thus the scattering associated with the peaks in $S(Q)$ is nearly elastic.

IV. CONCLUSION

The variational calculation shows that the ground state of the helium film corresponds to a compressed two-dimensional solid with the helium atoms exhibiting a high degree of localization. This localization rules out any exchange effects throughout the density range considered. The calculated density of monolayer completion is in excellent agreement with experiment, while the estimated Debye temperatures are in satisfactory agreement with experiment. These comparisons give strong support to this concept of the monolayer and to the concept of a Gauss-Hartree wave function being a good representation of the ground state. The pair-distribution function and structure factor are

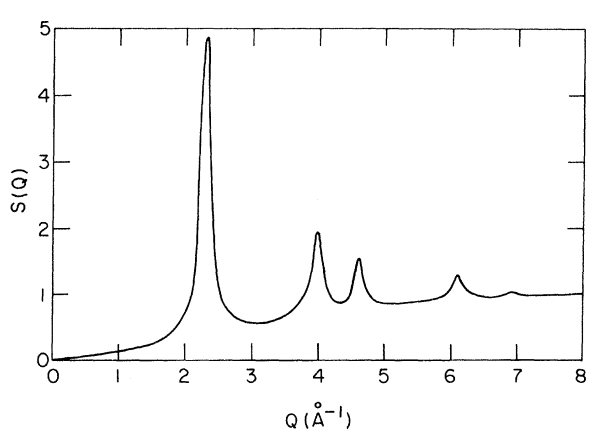

FIG. 6. Structure factor $S(Q)$ calculated with the modified pair-distribution function $\tilde{g}(r)$ for He^4, with $\rho = 0.116$ Å^{-2}. The value of γ is 0.09175 Å^{-2}.

calculated and await comparison to future neutron scattering experiments. Unless the substrate were to have a very strong disordering effect upon the monolayer, neutron scattering should give the monolayer lattice structure and the degree of localization of the helium atoms.

Generalizing these results, it would seem that the Gauss–Hartree approach to the ground state of the adsorbed film is quite reasonable. However, for certain substrates it might be necessary to incorporate a more detailed treatment of motion perpendicular to the surface.

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PHYSICAL REVIEW A VOLUME 7, NUMBER 2 FEBRUARY 1973

Mobilities and Longitudinal-Diffusion Coefficients of Mass-Identified Positive Ions in Carbon Monoxide Gas*

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We have measured with a drift-tube mass spectrometer the mobilities of CO$^+$, CO$^+\cdot$CO, and C$^+$ ions in carbon monoxide gas at 300 °K. The measurements were made over a substantial range of E/N, where E is the drift-field intensity and N is the gas number density. Zero-field reduced mobilities were determined for CO$^+\cdot$CO and C$^+$ ions. Their values are 1.90 ± 0.03 and 2.7 ± 0.1 cm^2/V sec, respectively. Measurements were also made of the longitudinal-diffusion coefficient of CO$^+$ ions in CO at 300 °K as a function of E/N.

I. INTRODUCTION

This paper presents the results of an investigation of the drift and longitudinal diffusion of low-energy positive carbon monoxide ions in carbon monoxide gas at room temperature. The data were obtained with a drift-tube mass spectrometer of ultrahigh-vacuum construction. The mobility of CO$^+$, CO$^+\cdot$ CO, and C$^+$ ions in CO and the longitudinal-diffusion coefficient of CO$^+$ in CO were determined as a function of E/N. The results are an extension of similar studies on H$_2$,[1,2] D$_2$,[2] N$_2$,[3,4] O$_2$,[5] and NO[6] performed in this laboratory. The only previous data[7] on the mobility of CO$^+$ and CO$^+\cdot$ CO ions in CO obtained with a drift-tube mass spectrometer apparently were seriously affected by the ion-molecule reaction

$$\mathrm{CO^+ + 2CO \rightarrow CO^+\cdot CO + CO}\,. \qquad (1)$$

No previous measurements on diffusion of ions in CO have been reported. In the present study, the effect of reaction (1), as well as other reactions, has been carefully considered and accounted for. In Paper II, immediately following this paper, the results of a study of reaction (1) will be presented.

II. GENERAL

As a slow ion moves through a gas under the influence of a static uniform electric field, on the average it gains energy from the field between