PHYSICAL REVIEW E VOLUME 56, NUMBER 2 AUGUST 1997

Electron attachment to O_2 molecules in dense helium and argon gases

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(Received 13 February 1997)

The resonant attachment frequency ν_A of excess electrons to O_2 molecules in dense helium and argon gases has been measured by the time-of-flight method. Measurements in helium have been performed in the temperature range 50–150 K. ν_A shows two sharp peaks as a function of the host medium density N, as a result of the formation of $O_2{}^-$ ions in the fourth and fifth vibrational levels owing to the shift of the electron self-energy with N. The density of the maximum of the first peak exhibits a positive temperature dependence partially explained by a simple model in which a bubble is formed around the ion and the resulting free-energy variation is taken into account in the determination of the resonance energy. On the contrary, measurements carried out in argon at $T=162$ K in an extended density range $[(5-115)\times 10^{20}\ \mathrm{cm}^{-3}]$ give a completely different result, as ν_A monotonically increases as a function of density and does not show any peak. The analysis of argon data needs a much better knowledge of the impurity-solvent interaction and of the electron self-energy since a rough estimate shows that even in argon a peak should have been observed. [S1063-651X(97)08808-9]

PACS number(s): 51.50.+v, 34.80.Lx

I. INTRODUCTION

Electron attachment to molecular impurities in dense gases can give information on the energetics and the density of states of excess electrons in disordered systems. The case of oxygen is well studied. At low densities, the attachment process can be described by the so-called Bloch-Bradbury two-stage process [1]. In the first step, an unstable $O_2{}^-$ ion is formed in a vibrationally excited state. Then the excess energy is carried away by a stabilizing collision with a third body. This is assumed to be a host gas atom since the impurity concentration is very low. It is known that in vacuum the electron resonance energies of the two first accessible levels, on averaging over the spin-orbit split doublets, are $E_R^{(4)}=91$ and $E_R^{(5)}=207$ meV [2], corresponding to the fourth and fifth vibrational levels of the ion, respectively.

Early experimental evidence of resonant attachment to oxygen molecules in dense helium gas is due to Bartels [3], who observed a sharp maximum of the attachment frequency ν_A (the first peak) at a density $N_4\approx 30\times 10^{20}\ \mathrm{cm}^{-3}$ and the low-density side of the second peak at $T=77$ K. Since the thermal energy is just a few meV at the temperature of the experiment, it is believed that the most important contribution to the resonance energy comes from the self-energy V_0 of excess electrons. In low-density helium, V_0 is well approximated by the Fermi shift [4] $E_F(N)=(2\pi\hbar^2/m)aN$, where m is the electron mass, a the electron-helium scattering length, and N the helium number density. In fact, for He it is $a=0.63$ Å and $E_F(N_4)\approx E_R^{(4)}$.

Subsequently, Bruschi, Santini, and Torzo [5] carried out measurements of the first attachment peak in He at several temperatures in the range 50–100 K and observed an unexpected increase of the density N_4 of the maximum with temperature. The attachment frequency has also been measured in neon by Borghesani and Santini [6] at several T between 48 and 100 K. At the lowest T, where the accessible density range was larger, they observed two broad peaks of ν_A/N as a function of density. As in the case of He, the density of the maximum of the first peak increases with T.

We carried out measurements in an extended density range in He in order to investigate the second attachment peak, which has not been observed so far, and how it is related to the first one and to T. We also repeated measurements of the first peak in order to compare them with those of Bruschi *et al.*, who used a different technique, obtaining a reasonable agreement.

In a further attempt to investigate the attachment phenomenon in dense gases, we then switched to argon, a system with a very different electron-atom interaction. In argon, V_0 is negative and decreases with increasing density. Moreover, argon atoms have a much higher polarizability than helium atoms, yielding a stronger ion-solvent interaction. In fact, as it is shown below, the results for argon are completely different from those for helium and neon, as we did not see any peak in an extended density range.

II. EXPERIMENT

A. Apparatus

We have used the same apparatus as for the measurements of electronic and ionic drift mobilities in dense gases; see [7] and references therein for the details. We recall here only its most important features.

The drift space is delimited by two parallel plane electrodes kept at a distance d (1.0 or 0.5 cm). Electrons are extracted from the photocathode by means of a short UV light pulse produced by a Xe flashlamp and drift through the drift space toward the anode under the action of an external uniform electric field. The time of flight t_e and the attachment frequency ν_A can be obtained by analyzing the signal wave form induced in an external RC circuit by the electronic motion.

1063-651X/97/56(2)/2137(6)/$10.00

The high-pressure cell can withstand pressures up to 10 MPa, can be cooled down to 25 K, and is thermoregulated within 0.01 K. To remove impurities such as water vapor, carbon dioxide, hydrocarbons, and, at high densities, part of O_2, a liquid-N_2-cooled activated charcoal trap and an Oxisorb trap are used. The oxygen concentration is estimated to be $\leqslant 10^{-7}$ [8].

B. Signal wave forms

The current induced by the motion of charges through the drift time is integrated by a passive RC network in order to maximize the signal-to-noise ratio. The signal is then digitized and analyzed by a personal computer. Because of the attachment process, the number of free electrons in the drift space varies as $n(t)=n_0\exp(-\nu_A t)$, where n_0 is the number of electrons extracted from the photocathode. Since $RC\approx 50$ ms$\gg t_e$, the electronic signal wave form is given by

$$v_e(t)=v_T[1-\exp(-\nu_A t)]/A \quad \text{for } t\leqslant t_e, \tag{1}$$

where $v_T=-en_0/C$ and $A=\nu_A t_e$. For $t>t_e$, $v(t)=v_e(t_e)\exp[-(t-t_e)/RC]$ owing to the capacitor discharge.

Equation (1) is valid as long as the ions are much slower than the electrons. In high-density low-temperature helium, where electrons becomes localized [9], such a condition is no longer satisfied and the ionic contribution to the induced current has to be taken into account. In this case, the signal wave form is given by [10]

$$v_1(t)=v_T\left(\frac{t}{t_i}+\frac{W-1}{WA}[1-\exp(-\nu_A t)]\right)\text{for } 0\leqslant t\leqslant t_e, \tag{2}$$

$$v_2(t)=v_T\left(\frac{t}{t_i}+\frac{W-1}{WA}\left\{1-\exp\left[-\frac{WA}{W-1}\left(1-\frac{t}{t_i}\right)\right]\right\}\right)$$
$$\text{for } t_e\leqslant t\leqslant t_i, \tag{3}$$

where t_i is the ionic drift time and $W=t_i/t_e$. A few numerical techniques [8,11] have been developed to fit Eqs. (1)–(3) to the experimental signals in order to obtain the attachment frequency ν_A.

C. Method

Measurements are taken along isotherms. The cell is filled at the highest pressure and at the purity degree required in a given run at the desired temperature. Lower densities are obtained by partly evacuating the cell. Before starting the measurement run we monitor ν_A until it is stationary to make sure that equilibrium is reached.

At each density, ν_A is measured as a function of the applied electric field in a range in which electrons are in thermal equilibrium with the gas atoms, as we can infer from the electron mobility, which is measured as well. In this range ν_A turns out to be nearly constant, within experimental accuracy. The error is estimated to be $\approx 5\%$.

For each isotherm, the cell has to be filled more than once at different impurity concentration because the attachment frequency can be measured with the best accuracy for $0.5<A<5$. Density ranges of different runs overlap each other in order to normalize the results.

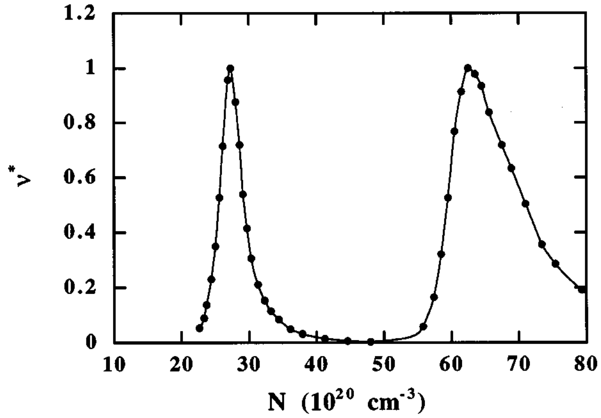

FIG. 1. Reduced attachment frequency ν^* in He at $T=54.5$ K as a function of density. The continuous line is only a guide for the eye.

III. EXPERIMENTAL RESULTS

In helium we have carried out measurements at $T=54.5$, 64.4, 77.2, 120.1, and 152.3 K. The maximum density reached at each temperature depends on the maximum pressure the cell can withstand. For this reason, at the three lowest temperatures we could observe two sharply defined peaks, whereas at higher T only the first peak could be measured.

The reduced and normalized attachment frequency $\nu^*=(\nu_A/N)/(\nu_A/N)_{max}$ as a function of density is shown in Fig. 1 for $T=54.5$ K and in Fig. 2 for $T=77.2$, 120.1, and 152.3 K. Data collected at $T=64.4$ and 77.2 K are very similar to those of Fig. 1. As shown in Fig. 3, the density of the maximum of the first peak increases linearly with temperature. On the contrary, we did not observe any clear temperature dependence of the maximum of the second peak, which seems to be nearly constant at $N\approx 62\times 10^{20}$ cm^{-3}. It has to be said that the accuracy of the measurements of the second peak is worse than that of the first one because of the presence of localized electrons.

Figure 4 shows the measured peak width ΔN at half

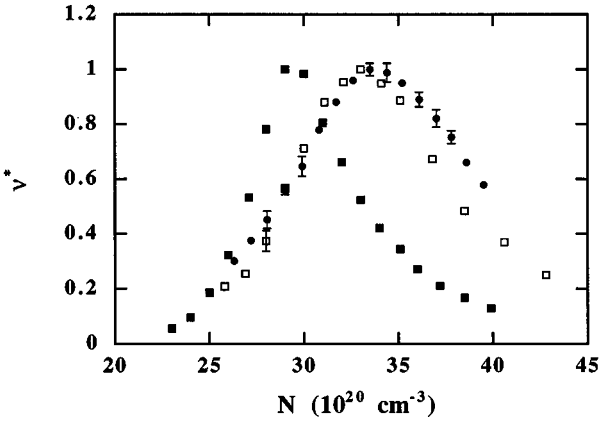

FIG. 2. Reduced attachment frequency ν^* in He at $T=77.2$ (closed squares), 120.1 (open squares), and 152.3 K (closed circles).

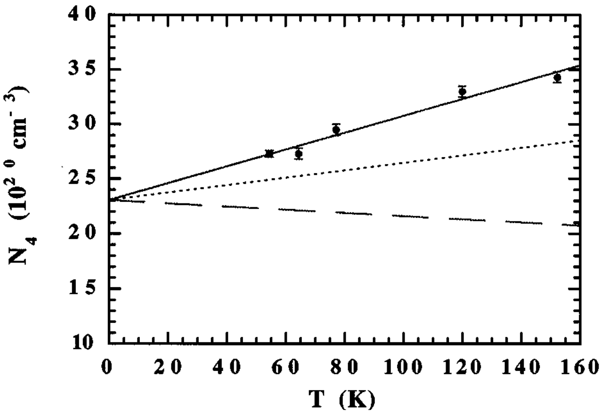

FIG. 3. Density of the maximum of the first attachment peak in He as a function of T. Circles, experimental results; continuous line, best fit of the data, $N_4=(23+0.077T)\times10^{20}$ cm^{-3}; dotted line, ionic bubble model; dashed line, Eq. (10).

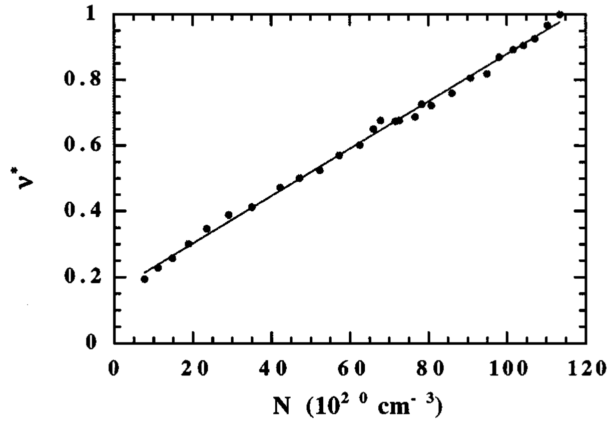

FIG. 5. Reduced attachment frequency ν^* in Ar at $T=162$ K as a function of density. $\nu^*=0.16+0.0072N$, with N in units of 10^{20} cm^{-3}.

height as a function of temperature. It increases linearly with T in the case of the first peak (solid circles). The width of the second peak (solid squares), on the contrary, seems to decrease slightly.

Measurements carried out in argon have given a completely different result with respect to helium. At $T=162$ K and for $5<N<115\times10^{20}$ cm^{-3}, we did not observe any peak and ν^* increases linearly with N, as shown in Fig. 5.

IV. DISCUSSION

In discussing our measurements we will make the assumption that the vibrational levels of the oxygen ion and molecule do not change when they are immersed in a dense gas. At resonance the electron energy E must be equal to

$$E=(E_n-E_0)-E_A(N,T), \tag{4}$$

where E_n-E_0 is the vibrational excitation energy of O_2^- and $E_A(N,T)$ is the electron affinity of O_2 immersed in a gas of temperature T and density N. The quantities $E_R^{(n)}=(E_n-E_0)-E_A(N=0)=91$ or 207 meV, for $n=4$ and 5, respectively, are known. In the case of Ar, since the electron self-energy V_0 is negative, we have to consider also the third vibrational level, whose energy with respect to the ground state of the neutral oxygen molecule is estimated to be $E_R^{(3)}=E_R^{(4)}-120=-29$ meV. The value 120 meV is obtained by interpolating between $E_R^{(5)}-E_R^{(4)}=207-91=116$ meV and $E_1-E_0=135$ meV [12], the excitation energy of the first vibrational level of the ion.

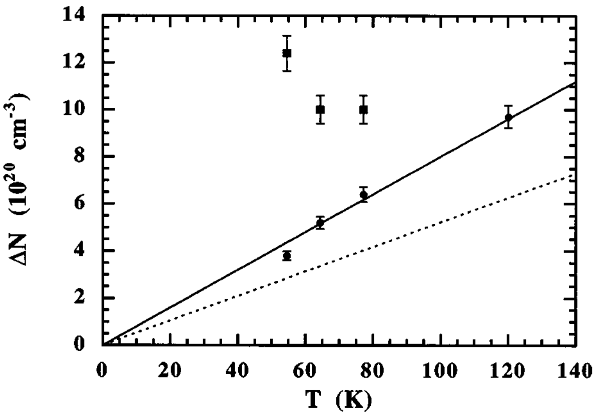

FIG. 4. Measured peak width ΔN at half height in He as a function of T. Circles, first peak; squares, second peak; continuous line, best fit of the first peak data; dotted line, classical shifted distribution calculated according to the Fermi model (see the text).

Hence, in order to calculate the electron resonance energy, the quantity $\Delta(N,T)=E_A(N,T)-E_A(N=0)$ is needed. As a first approximation, $\Delta(N,T)$ is due to polarization forces and can be estimated to be

$$\Delta(N,T)\approx\frac{\alpha e^2N}{2}\int\frac{g(\mathbf{r})S(\mathbf{r})}{r^4}d\mathbf{r}, \tag{5}$$

where α is the host gas atom polarizability, $g(\mathbf{r})$ is the O_2-atom pair correlation function, and $S(\mathbf{r})\approx(1+8\pi\alpha N/3)^{-1}$ is the Lorentz screening function [13].

A rough estimate of $\Delta(N,T)$ is obtained using a fcc lattice model in which the oxygen molecule is taken to be a substitutional impurity [13]

$$\Delta(N)\approx\frac{\alpha e^2}{2}\left(\frac{N}{\sqrt{2}}\right)^{4/3}\left(1+\frac{8}{3}\pi\alpha N\right)^{-1}\times25.34, \tag{6}$$

where the last factor is given by a sum over the lattice sites. At $N=30\times10^{20}$ cm^{-3}, $\Delta(N)\approx10$ meV for helium and ≈80 meV for argon.

The attachment frequency ν_A is given by [5]

$$\nu_A=p_s\sigma_cN_2v(E_R)F(E_R,N), \tag{7}$$

where p_s is the stabilizing coefficient, σ_c is the integrated capture cross section, N_2 is the impurity (oxygen) density, and $v(E_R)$ and $F(E_R,N)$ are the electron velocity and distribution function at the resonance energy E_R. We assume that the capture cross section σ_c and the stabilizing coefficient p_s do not vary much with density. Since $N_2=CN$, where C is the constant and unknown oxygen concentration, we finally have

$$\nu_A/N\propto F(E_R,N). \tag{8}$$

Excess electrons are immersed in a dense medium and have a self-energy $V_0(N)$. Let us consider a simple model in which, neglecting density fluctuations, the effect of the self-energy is that of shifting the classical Maxwell distribution by an amount V_0. The most probable electron energy is $E_M = V_0 + k_B T/2$ and ν_A/N therefore has a maximum at a density $N = N_M$ for

$$E_M = V_0(N_M) + k_B T/2 = E_R^{(n)} - \Delta(N_M, T). \tag{9}$$

Helium has a low polarizability and hence, as a first approximation, $\Delta(N,T)$ can be neglected. Moreover, at low N, $V_0(N) \approx bN$. In fact, we observe that the second-to-first peak maximum density ratio at 54.5 K, $r = 2.26 \pm 0.01$, is equal to the ratio between the resonance energies 207/91 $= 2.27$. However, this is true only at 54.5 K. At $T = 77$ K it is $r = 2.07 \pm 0.02$, as the density of the maximum of the first peak increases with T, while that of the second one remains nearly constant.

It can be seen [5] that, according to this simple model, the width ΔN at half height is given by $1.8 k_B T/b$. From the linear fit of the data shown in Fig. 4, we obtain $b = 1.93 \times 10^{-20}$ meV cm^3. As a comparison, the Fermi model gives $b_F = (2\pi\hbar^2/m)a = 2.97 \times 10^{-20}$ meV cm^3. This could mean that, even though the Fermi model gives a good estimate of the amount of the shift of $F(E_R, N)$, the real electron distribution function is wider because of density fluctuations.

The width at half height of the second peak does not show the same behavior and decreases as T increases. We believe that this could be due to the presence, at lower T, of a greater amount of localized electrons self-trapped in a bubble state [14], whose energy $E_B \ll V_0$. In this case, when the density is greater than that of the maximum and hence $V_0 \gg E_R$, there still exists a considerable fraction of electrons in the bubble state that have a mean energy $E_B \approx E_R$. In such a way the attachment frequency is still large, yielding a peak wider than at higher T, where the amount of trapped electrons decreases.

The density of the maximum of the first peak N_M should decrease with increasing T since there is a greater thermal contribution to the electron energy

$$N_M = \left(E_R - \frac{1}{2} k_B T \right) \frac{1}{b} \tag{10}$$

(dashed line in Fig. 3). Experimentally, the behavior is quite the opposite, in agreement with the results of Bruschi *et al.* [5].

Before presenting a simple model in order to partially explain this apparently strange behavior, we discuss the case of argon. In argon V_0 is negative and decreases with density to reach a broad minimum at $N \approx 125 \times 10^{20}$ cm^{-3} [15]. Moreover, $\Delta(N,T)$ is no longer negligible. As shown in Fig. 6, the resonance condition (9), is reached for the fourth level at $N \approx 90 \times 10^{20}$ cm^{-3}. Hence, according to this simple model, an attachment peak should have been observed at about this density, but it is not. However, it must be remembered that V_0 is known with poor accuracy and $\Delta(N,T)$ is just a rough estimate. Therefore, an uncertainty of a few tens of meV in these quantities can give a resonance condition at a much different N.

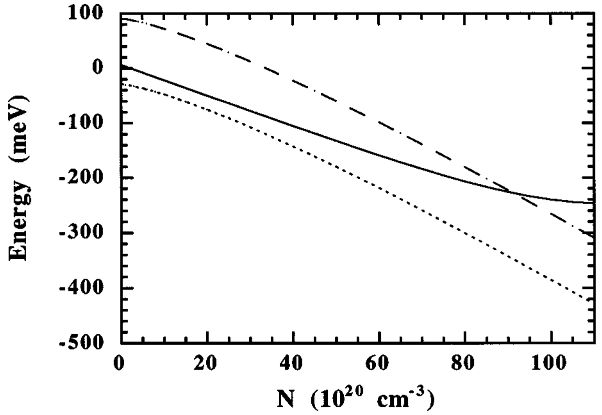

FIG. 6. Resonance condition (9), calculated in Ar at $T = 162$ K as a function of N for the third and fourth vibrational levels. Continuous line, $V_0 + k_B T/2$; dashed line, $E_R^{(4)} - \Delta(N,T)$; dotted line, $E_R^{(3)} - \Delta(N,T)$.

We also point out that a more refined model should consider density fluctuations and a consequent broadening of the electron distribution function. In this way the peaks might be much wider and large attachment frequencies could be observed even though the resonance condition is not fully satisfied by the most probable state of the electrons. Moreover, since argon is much heavier than helium, we can also suggest that the interaction of the O_2 molecule with argon atoms might modify the vibrational levels in a still unknown way that might invalidate the use of the resonance energies measured in vacuum.

The dependence of the first peak with *T* in He

Khrapak, Schmidt, and Volykhin [16] have recently proposed a model of the structure of O_2^- ions in dense helium gas that takes into account the repulsive interaction of the outer electron of the ion with the surrounding helium atoms. They have shown that an empty void is created around the ion, in analogy with the case of excess electrons. This is due to the fact that the outer electron is localized in a spatial region with a size greater than that of the electron shells of the oxygen molecule.

Khrapak *et al.* start considering the case of an isolated O_2^- ion, whose main properties can be described by a simple model potential between the outer electron and the neutral oxygen molecule: $V(r) = -\alpha e^2/2r^4$ for $r > R_0$ and $V(r) = \infty$ for $r \leq R_0$. R_0 is the effective radius of the short-range hard-core potential and $\alpha = 1.57$ Å^3 is the polarizability of the oxygen molecule. The hard-core radius $R_0 = 0.48$ Å is obtained by solving the Schrödinger equation with eigenenergy equal to the electron affinity of oxygen in vacuum, $E_A(N=0) = 460$ meV.

Then they consider the possibility of creating an empty spherical void of radius R when the ion is immersed in dense helium gas, treated as a continuum. The repulsive interaction of the outer electron of the ion with helium atoms is described in terms of the self-energy V_0. The potential $V(r)$ now takes the form

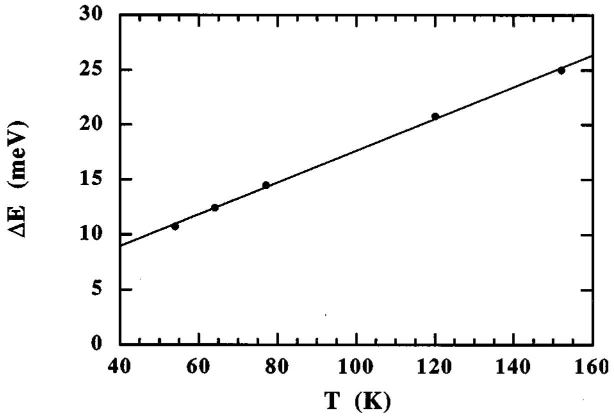

FIG. 7. Energy shift ΔE as a function of T calculated according to the ionic bubble model. The line is the linear fit of the data.

$$V(r)=\begin{cases} V_0-\alpha e^2/2r^4 & \text{for } r\geqslant R \\ -\alpha e^2/2r^4 & \text{for } R_0<r\leqslant R \\ \infty & \text{for } r\leqslant R_0, \end{cases} \tag{11}$$

where the hard-core radius R_0 is the same as calculated before. The equilibrium radius R_B is obtained by minimizing the free-energy variation ΔF, due to the formation of the bubble, with respect to the radius R

$$\Delta F(R)=-\epsilon(R)+\frac{4}{3}\pi PR^3+4\pi\sigma R^2, \tag{12}$$

where $\epsilon(R)$ is the electron energy, P the pressure, and σ the surface tension. It is found that the cavity radius does not depend on the density and is a decreasing function of temperature.

We have applied this model to our measurements of attachment frequency in the following way. In the energy balance one also has to consider the energy necessary to create the bubble around the ion, as the duration of the attachment process [17] and the time for the formation of the bubble [18] are of the same order of magnitude. This energy is supplied by the electron. Since the ground state of the electron in the model of the ionic bubble is shifted with respect to the case of the isolated ion, we assume that the vibrational levels are shifted by the same quantity. That means that the resonance energy is now given by $E_R^{(n)}+\Delta E$, where $\Delta E=-E_A(N=0)+\Delta F(R_B)$.

We have calculated ΔE as a function of T in helium at the density of the maximum of the first peak, by solving numerically the Schrödinger equation with the potential $V(r)$ given by Eq. (11) [8]. The interesting result, reported in Fig. 7, is that ΔE increases linearly with T, $\Delta E=(\Delta E)_0+pT$, with a slope $p=0.145$ meV/K. This implies an increase of the density of the peak maximum, as we observed in our measurements.

We estimate this increase as follows. Using the Fermi model $V_0=bN$ and still neglecting $\Delta(N,T)$, we now write the resonance condition (9), modified according to the ionic bubble model, as

$$bN_4(T)+k_BT/2=E_R^{(4)}+(\Delta E)_0+pT, \tag{13}$$

from which we have

$$N_4(T)=N_4(0)+\frac{p-k_BT/2}{b}T=N_4(0)+p_NT. \tag{14}$$

The value $p_N=0.034\times10^{20}$ cm^{-3}/K is to be compared with the experimental one, 0.077×10^{20} cm^{-3}/K.

The agreement is satisfactory, given the crudeness of the model. Figure 3 shows the linear fit of the experimental data (continuous line), the result of the ionic bubble model (dotted line), and the result of Eq. (10) (dashed line). Since our reasoning concerned only the slopes, we have forced the two theoretical lines to meet the experimental fit for $T=0$.

V. CONCLUSION

We have presented experimental measurements of attachment frequency in dense helium and argon gases. In helium, we have observed the complete attachment peak due to the formation of the ion in the fifth vibrational level. The density of the maximum of the first peak increases with T, in agreement with previous measurements of Bruschi *et al.* This dependence, which at first may seem unexpected, is qualitatively explained by means of the ionic bubble model, proposed by Khrapak *et al.* Finally, we report measurements of attachment in dense argon, where the attachment frequency does not exhibit any peak and increases monotonically with N. The analysis of argon data lacks an accurate knowledge of V_0 and $\Delta(N,T)$.

In summary, the measurement of the attachment frequency is a powerful tool to investigate the states of excess electrons in a disordered medium, but there are still unsolved questions, as we did not observe the doublet spin-orbit structure in any peak and it is not known how the vibrational levels of the oxygen might be modified when the molecule is immersed in a dense medium. We hope that these measurements will stimulate further theoretical and experimental work on this subject.

ACKNOWLEDGMENTS

We wish to thank Giorgio Delfitto for technical support. D.N. acknowledges partial support by the Istituto Nazionale per la Fisica della Materia under Grant No. 1685/96/UDR-PADO-PER.

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