

DENSITY AND TEMPERATURE DEPENDENCE OF ELECTRON ATTACHMENT TO O₂ MOLECULES IN HELIUM GAS[☆]

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The electron attachment frequency to O₂ molecules in dense helium gas shows a sharp peak at a temperature-dependent density N_p . The shape of the peak is simply related to the energy distribution function, and gives information on the tail states.

We have studied the resonant attachment of excess electrons to O₂ molecules in dense helium gas, with the aim of gaining information on the electron energy distribution function. The capture via non-dissociative attachment has been well studied in the past, and it can be described as a two-stage process [1]. The electron is first captured to form a vibrationally excited temporary ion, which is later collisionally stabilized into the ground state.

The first stage is a resonant capture, which occurs only when the colliding electron has some discrete energies E_n . In the present experiment we are dealing with the first accessible resonance $E_R = 0.091$ eV. The measurements were made in the temperature range 50–100 K, and at helium number densities N in the range $(2-5) \times 10^{21}$ cm⁻³. The oxygen concentration C was very low, $C \approx 3 \times 10^{-8}$, and the excess electron number density n was about 1×10^4 cm⁻³.

The method of measurement of the attachment frequency ν_A is derived from a modified version of the square-wave method (SWM) used in the past for the measurement of the ionic mobility [2]. A radioactive source (5 mCi, ⁶³Ni, Radiochemical Centre Amersham) ionizes the fluid near the emitter electrode S, which is kept at negative potential with respect to

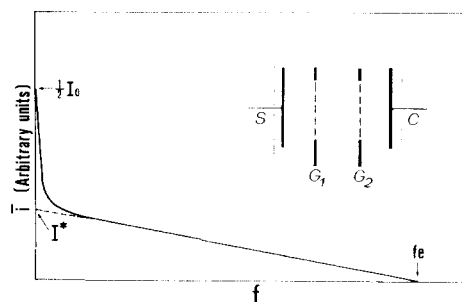


Fig. 1. The collector current as a function of frequency for the physical situation specified in the text. In the upper inset a schematic of the measuring cell.

the first grid G_1 (fig. 1). This electrode is reached by the negative charges extracted from the ionization region (both free electrons and O₂⁻ ions produced in between S and G_1 by the attachment process). The grid G_1 is driven with respect to the second grid G_2 by a square-wave signal V_1 at a frequency f_1 such that only the electrons can reach G_2 , while the much slower ions entering through G_1 , and those created between G_1 and G_2 , are left behind. The grid G_2 acts as a pulsed pure electron injector of a mean current I_0 [3]. The grid G_2 is driven, with respect to the collector C, by a positive and negative square-wave voltage V_2 of frequency f , as in SWM [2].

The mean current \bar{I} collected at C is a function of the frequency f , and the behaviour depends strongly

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on the ratio $R = \mu_e/\mu_i$ between electronic and ionic mobilities, and on the efficiency of the attachment process. A sketch of the calculated \bar{t} as a function of f is shown in fig. 1, for a situation such that $R = 100$, and $t_{ML} = t_e$, where $t_{ML} = 1/\nu_A$ is the mean life of the free electrons, and t_e is their time of flight from G_2 to C. At zero frequency $\bar{t} = I_0/2$, where the mean injected electronic current I_0 is measured driving G_2 with a dc voltage V_0 exactly equal to the negative amplitude of the square wave V_2 . At high frequency, \bar{t} is linear with f , $\bar{t} = I^*(1 - f/f_e)$ as in the square-wave method, and the cutoff frequency f_e gives the electronic time of flight, $t_e = 1/2f_e$. The electronic contribution I^* to the collected current at zero frequency is smaller than $I_0/2$ because the beam is attenuated by the attachment process. It is easy to show that the attachment frequency is given by

$$\nu_A = 2f_e \ln(I_0/2I^*).$$

The ionic charges between G_2 and C are swept back to G_2 by a suitable polarization of the square wave V_2 [3].

We used small electric fields, typically 100 V/cm, so that the drift velocity was typically $v_D \approx 5 \times 10^3$ cm/s. In such a condition our method requires O_2 concentrations of the order of 10^{-8} [3]. At this low level it was impossible to use an impurity content measured with enough confidence. The "high purity" gas was therefore introduced into the cell via a cold charcoal trap to remove the oxygen content down to the appropriate value, and the measurements were taken while decreasing the pressure. In this way we worked with an unknown but constant impurity concentration. The values of ν_A measured at $T = 44.5$ K are plotted in fig. 2 versus the helium number density N . The attachment frequency shows the characteristic peak first discovered at 77 K by Bartels [4], whose results are in very good agreement with our measurements at the same temperature.

The existence of the peak is easily understood if we remind that the main contribution to the electron energy is the self energy E_0 , due to electron-scatterers interaction, while the thermal energy is only a minor part. At low densities E_0 is approximated by the Fermi shift relation,

$$E_0 = (2\pi\hbar^2/m)Na = bN,$$

where m is the electron mass and a is the scattering

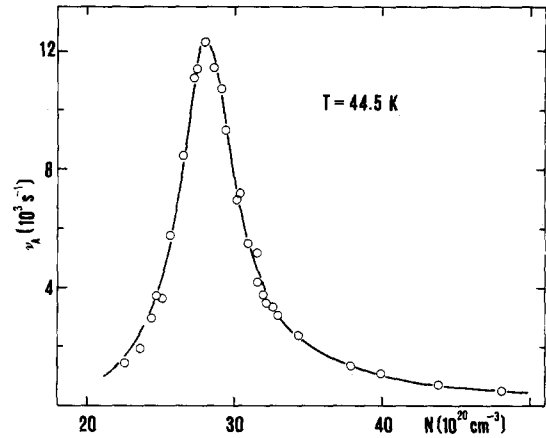


Fig. 2. The attachment frequency ν_A versus the helium density N , measured at $T = 44.5$ K as explained in the text.

length [5]. We should expect a maximum ν_A when $E_0 \approx E_R$, at a density $N_R \approx E_R/b$. The results obtained at $T = 77$ K [4] are well explained by this qualitative picture, but our measurements at lower and higher temperatures show a more complicated situation.

It is easily shown by elementary kinetic calculations, that

$$\nu_A = N_2 p_s \sigma_c v(E_R) F(E_R, N),$$

where N_2 is the O_2 number density, σ_c the integrated capture cross section, $v(E_R)$ and $F(E_R, N)$ are the electron velocity and the energy distribution function at $E = E_R$ [3], and p_s is the probability for the temporary ion to be collisionally stabilized into the ground state. The effective integrated attachment cross section $\sigma_A = p_s \sigma_c$ is believed to be proportional to N [1, 4]. In our experiments $N_2 = CN$, where the concentration C is kept constant, and therefore ν_A/N^2 has the same density dependence as $F(E, N)$ at $E = E_R$. The quantity ν_A/N^2 , when plotted versus N , shows a peak with a maximum at a density N_p , which increases with temperature. The data in the temperature range 45–100 K are well fitted by the linear relation

$$N_p = (2.36 + 8.8 \times 10^{-3} T) \times 10^{21} \text{ cm}^{-3}.$$

This is surprising because we expect a smaller contribution to be needed when the thermal contribution is greater. If we calculate the self energy E_0 with the Wigner-Seitz model [6], using $a = 0.62$ Å for the

scattering length, we find that E_0 reaches the value E_R at a density $N_R = 2.37 \times 10^{21} \text{ cm}^{-3}$, the same value one obtains extrapolating the measured N_p at zero temperature. At $T \neq 0$ one needs a mean density N greater than N_R to bring the extra electron into resonance. This suggests a local density decrease around the electron, as a result of the electron–helium interaction, an effect linearly increasing with temperature.

The resonance peak has a characteristic temperature-dependent shape related to the density of states $g(E, N)$. In the temperature range investigated, the peak width ΔN , taken for example at half height, is proportional to T . The results are fitted by the relation $\Delta N = (8.8 \times 10^{18} T) \text{ cm}^{-3}$, or in terms of energy (using the relation $\Delta E = b \Delta N$) $\Delta E = 3.0 k_B T$, where k_B is the Boltzman constant. The most simple density of states we can use to get a peak shape, is

$$g(E) = A(E - E_0)^{1/2},$$

with

$$A = (V/2\pi^2)(2m/\hbar^2)^{3/2},$$

where V is the volume of the sample, and $E_0 = bN$ is the electron self energy. The energy distribution function at $E = E_R$,

$$F(E_R, N) = [g(E_R, N)/Z(N)] \exp(-E_R/k_B T),$$

yields

$$F(E_R, N) = D(E_R - bN)^{1/2} \exp[-(E_R - bN)/k_B T],$$

where

$$D = (2\pi^{-1/2})(k_B T)^{-3/2}.$$

It is the free electron distribution function, simply shifted by an amount E_0 . It has a sharp edge at $E = E_0$, an unrealistic picture. The helium density in fact is sensed in a rather small volume $V^* \approx (\Delta x)^3$, where Δx is the spatial extent of the electron wave packet, $\Delta x \approx 40 \text{ \AA}$ at $E = E_R$. The self energy fluctuates therefore around a mean value because of the density fluctuations, and $g(E)$ must have a tail around E_0 , a typical feature of the disordered systems.

Nevertheless we found that this simple energy distribution, at the lower-density side of the peak, fits well the data up to the maximum, whereafter it falls rapidly to zero because it neglects the density fluctuations. This shows that at the lower side of the peak we are dealing with essentially extended states, while the high-density side is representative of the tail states related to the fluctuations of the Wigner–Seitz potential. The resonant capture by molecular impurities can therefore be used to get unique informations on the density of states, and it can be an important and direct test for the theories, and a means for a deeper understanding of the disordered systems.

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