

## **Kinetic Theory Analysis of Electron Attachment Cooling in Oxygen**

*H. R. Skullerud*

Electron and Ion Physics Research Group,  
Physics Department, Norwegian Institute of Technology,  
N7034 Trondheim, Norway.

### *Abstract*

The attachment cooling effect observed by Hegerberg and Crompton (1983) has been analysed theoretically and numerically in a Boltzmann equation eigenvalue approach. The effect is highly sensitive to the shape and magnitude of the rotational excitation cross sections. When due account is taken of the rotational excitations associated with the ( $O_2^-$ ) negative ion resonances, good agreement between theory and experiment can be obtained with reasonable input cross-section data.

### **1. Introduction**

Hegerberg and Crompton (1983; present issue p. 831) have recently studied diffusion and attachment of thermal electrons in  $O_2$  and in  $O_2-N_2$  mixtures by measuring the asymptotic decay time of the electron density in a diffusion cell, using the Cavalleri detection technique. The experiments were performed at room temperature, with total pressures in the range from 0.5 to 3 kPa.

The observed decay times were longer than those calculated from reported values of the electron diffusion coefficient (Nelson and Davis 1972) and the three-body attachment rate coefficient (Shimamori and Hatano 1976, 1977). The disagreement increased with increasing  $O_2$  density, and was reduced by the addition of  $N_2$ .

The appearance of these anomalously long decay times is caused by the energy-selective removal of electrons by attachment at a rate faster than the typical energy relaxation rate. This distorts the electron energy distribution from the Maxwellian form, and reduces the effective attachment rate (Crompton *et al.* 1980).

Shimamori and Hatano (1976, 1977) and Shimamori and Fessenden (1981), on the other hand, did not observe any 'attachment cooling' effect in experiments in pure  $O_2$  at pressures up to 110 Torr (1 Torr  $\equiv$  133 Pa). The reason for this is presently not understood. It is noteworthy, however, that the presence of small amounts of  $H_2O$ , which is a very effective electron thermalizer, can remove the attachment cooling effect completely (Hegerberg and Crompton 1983).

In the present paper, a kinetic theory analysis of the attachment cooling effect in  $O_2$  is given. The treatment is largely based on studies by Leemon and Kumar (1975) and Robson (1976) of the related diffusion cooling effect.

A main difficulty in the calculation of low energy electron swarm behaviour in  $O_2$  is the lack of reliable cross-section data in the thermal energy region. Both elastic and direct rotationally inelastic cross sections are uncertain by a factor of order 2, and the position of the negative ion resonances (a huge number of narrow lines spread

over an energy range of order 50 meV) is uncertain by about  $\pm 15$  meV. We have selected a set of cross sections which gives reasonable agreement with experiment, but there are too many unknown parameters to make the set unique. The selection of cross sections will be discussed in some detail.

## 2. Low Energy e-O<sub>2</sub> Collision Processes

In the thermal energy range,  $E \lesssim 100$  meV, three distinct processes contribute to e-O<sub>2</sub> scattering. These processes are elastic scattering, direct rotationally inelastic scattering, and resonant scattering via a vibrationally excited and autoionizing (O<sub>2</sub><sup>-</sup>)<sub>v=4</sub> negative ion state.

The resonant scattering process has both elastic, rotationally inelastic and rotationally superelastic channels. In addition, it may be interrupted by interaction with a third body, in which case the end product may become a stable negative ion (O<sub>2</sub><sup>-</sup>)<sub>v<4</sub>. This negative ion formation process, first suggested by Bloch and Bradbury (1935), appears to be the dominant attachment process in oxygen at temperatures around 300 K and pressures below 20 kPa (Shimamori and Fessenden 1981, and references therein).

### Direct Elastic Scattering

Chang (1981) has used modified effective range theory to derive expressions for both total and momentum transfer cross sections for electron scattering from homopolar molecules. These expressions can be written in the form

$$\sigma = \sigma_0(1 + a_1 k + a_2 k^2 \ln k + a_3 k^2), \quad (1)$$

where  $k = (2mE)^{1/2}/\hbar$ .

Lawton and Phelps (1978) have made a careful selection of e-O<sub>2</sub> cross sections over the energy range from 0.01 to 100 eV. In the range 0.01–0.05 eV, they recommended a momentum transfer cross section  $\sigma^{(1)}$  approximately proportional to  $k$  (see also Hayashi 1981):

$$\sigma^{(1)} \approx 0.7(E/0.01 \text{ eV})^{1/2} \text{ \AA}^2 \quad (0.01 < E < 0.05 \text{ eV}). \quad (2)$$

If equation (2) is used to calculate the product of gas density and diffusion coefficient,

$$n_0 D = \frac{1}{3} \langle v/\sigma \rangle, \quad (3)$$

a value of  $2.8 \times 10^{24} \text{ m}^{-1} \text{ s}^{-1}$  results. This is considerably lower than the experimental values found by Nelson and Davis (1972) and by Hegerberg and Crompton (1983),  $(4.2 \pm 0.4) \times 10^{24} \text{ m}^{-1} \text{ s}^{-1}$  and  $(3.7 \pm 0.3) \times 10^{24} \text{ m}^{-1} \text{ s}^{-1}$  respectively, and the recommended cross section of equation (2) is consequently too high.

At the present time, sufficient experimental information does not exist to fix the parameters in equation (1). For lack of better alternatives, we have therefore chosen to use below 50 meV the cross section

$$\sigma^{(1)} = \sigma_0(1 + a_3 k^2) = (0.30 \text{ \AA}^2)(1 + E/0.0195 \text{ eV}), \quad (4)$$

and at higher energies the cross section of Lawton and Phelps (1978). This gives a diffusion coefficient in agreement with the measured value of Hegerberg and Crompton (1983), but there is no reason to believe that the shape chosen has much to do with reality.

### *Direct Rotationally Inelastic Scattering*

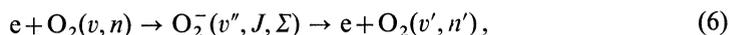
Rotational transitions, with a change  $\Delta n = \pm 2$  in the rotational quantum number  $n$ , are induced by long-range quadrupole forces modified by polarization, and to a less well-known extent by short-range forces. For  $O_2$ , the quadrupole moment  $Q$  is approximately  $0.30ea_0^2$ , which is quite small compared with other homopolar molecules. As a result, both short-range forces and polarization forces will be of importance, while for other molecules they can often, to a good approximation, be neglected. Nevertheless, we will here only take the quadrupole forces into account, and use the quadrupole Born cross section of Gerjuoy and Stein (1955)

$$\sigma(n \rightarrow n+2) = \frac{8\pi k'}{15 k} \frac{(n+1)(n+2)}{(2n+1)(2n+3)} (Q/ea_0)^2. \quad (5)$$

It is known how the polarization forces will modify this cross section (Takayanagi and Itikawa 1970), but this modification is counteracted by the short-range forces—to an extent presently unknown.

### *Resonant Scattering and Attachment*

The resonant scattering proceeds via the formation and subsequent break-up of an  $O_2^- \ ^2\Pi_g$  ion:



where  $v, v'$  and  $v''$  are vibrational quantum numbers,  $n$  and  $n'$  are rotational quantum numbers,  $J$  is a total angular momentum quantum number, and  $\Sigma = \pm \frac{1}{2}$  is a spin quantum number corresponding to the fine-structure states

$$\Omega = \Lambda + \Sigma = (\frac{1}{2}, \frac{3}{2}).$$

Linder and Schmidt (1971) measured angular spectral cross sections  $\sigma_{\Omega, E}$  for the process (6) in a beam experiment with electrostatic energy analysis. The measurements located the lowest resonance ( $v = v' = 0, v'' = 4$ ) at  $76 \pm 20$  meV, and the next resonance ( $v = v' = 0, v'' = 5$ ) at  $201 \pm 20$  meV, and showed the resonant scattering to be nearly isotropic. The energy resolution was not sufficient to see the spin-orbit splitting or the individual rotational levels.

Land and Raith (1974) measured total e- $O_2$  scattering in a time-of-flight absorption experiment, and found the lowest resonance to have fine-structure peaks  $20 \pm 2$  meV apart, with the midpoint between the peaks at  $91 \pm 5$  meV. The individual rotational levels were not resolved, and cross sections were not reported.

Fiquet-Fayard (1975) and Parlant and Fiquet-Fayard (1976) treated the e- $O_2$  scattering theoretically in a pure resonant scattering approximation. We shall here give a short survey of their findings with respect to the lowest resonance, with some slight extensions.

For symmetry reasons, the allowed partial waves are  $l = 2, 4, \dots$ , and at low energies, only the  $l = 2$  partial wave needs to be accounted for. Each initial rotational state  $n$  ( $= 1, 3, 5, \dots$ ) can give rise to six different negative ion  $J$  values ( $n - \frac{5}{2} \leq J \leq n + \frac{5}{2}$ ) for each fine structure state  $\Sigma = \pm \frac{1}{2}$ . This yields 12 resonances per  $n$  value, located

at energies

$$E(nJ\Sigma) = B''J(J+1) - B'n(n+1) + E_0 \quad (\Sigma = -\frac{1}{2}), \quad (7a)$$

$$E(nJ\Sigma) = B''J(J+1) - B'n(n+1) + E_0 - \Delta E \quad (\Sigma = +\frac{1}{2}), \quad (7b)$$

where  $B' \approx 1.792 \times 10^{-4}$  eV and  $B'' \approx 1.45 \times 10^{-4}$  eV are the rotational constants of  $O_2$  and  $O_2^-$  respectively, and  $\Delta E \approx 0.020$  eV is the spin-orbit splitting. The resonance position measured by Linder and Schmidt (1971) corresponds to  $E_0 \approx 0.086$  eV, while the value of Land and Raith (1974) corresponds to  $E_0 \approx 0.100$  eV.

The relative magnitudes of the energy-integrated cross sections for each resonance are given by angular momentum coupling rules and the linewidths  $\Gamma(E)$  which are approximately proportional to  $E^{5/2}$ . The linewidths are small compared with the electron energy ( $\Gamma \lesssim 10^{-4}$  eV) and the cross sections can therefore, for our purposes, be replaced by  $\delta$  functions at the resonance energies. One thus obtains

$$\sigma(J\Sigma | n) \propto \{E(nJ\Sigma)^{3/2} B(J\Sigma | n) / \tilde{\Gamma}(J\Sigma)\} \delta(E - E(nJ\Sigma)); \quad (8)$$

$$\begin{aligned} B(J\Sigma | n) = & \sum_j \sum_p \sum_{\sigma \sigma'} (\frac{1}{2}\sigma_e 1\sigma | \frac{1}{2}\Sigma) (\frac{1}{2}\sigma_e' 1\sigma | \frac{1}{2}\sigma) \\ & \times (\frac{1}{2}\sigma_e j\sigma | p\Sigma) (\frac{1}{2}\sigma_e' j\sigma' | p\sigma) |(p\Sigma 21 | J(1+\Sigma))|^2 \\ & \times (1\sigma n 0 | j\sigma) (1\sigma' n 0 | j\sigma') (2n+1)/(2j+1), \end{aligned} \quad (9)$$

$$\begin{aligned} \tilde{\Gamma}(J\Sigma) = & \sum_{n'} (2n'+1) E(n'J\Sigma)^5 B(J\Sigma | n') \\ & \times \left[ \sum_{n''} (2n''+1) E(n''J\Sigma)^{5/2} B(J\Sigma | n'') \right]^{-1}. \end{aligned} \quad (10)$$

In equation (9), the quantities  $(j_1 m_1 j_2 m_2 | j_3 m_3)$  are Clebsch-Gordan coefficients,  $(\sigma_e, \sigma_e') = \Sigma - (\sigma, \sigma') = \pm \frac{1}{2}$ , and the summation ranges are  $n-1 \leq j \leq n+1$ ,  $j-\frac{1}{2} \leq p \leq j+\frac{1}{2}$ ,  $-1 \leq \sigma \leq 1$  and  $-1 \leq \sigma' \leq 1$ . In equation (10), the summation range is  $J-\frac{3}{2} \leq n' \leq J+\frac{3}{2}$ .

From microscopic reversibility, one also finds that the total cross sections for transitions  $n \rightarrow J\Sigma \rightarrow n'$  are

$$\begin{aligned} \sigma(n' \leftarrow n) = & \sigma(J\Sigma | n) (2n'+1) E(n'J\Sigma) B(J\Sigma | n') \\ & \times \left( \sum_{n''} (2n''+1) E(n''J\Sigma) B(J\Sigma | n'') \right)^{-1}. \end{aligned} \quad (11)$$

For a given  $J$  value, three (odd) values of  $n'$  and  $n$  are possible,  $(n, n') = n_0(J), n_0(J) \pm 2$ . If  $n = n_0(J)$ , then  $n'$  can have the values  $n$  and  $n \pm 2$ ; if  $n = n_0(J) - 2$ ,  $n'$  can have the values  $n, n+2, n+4$ ; and if  $n = n_0(J) + 2$ ,  $n'$  can have the values  $n, n-2, n-4$ .

The attachment probability is (to lowest order in the density) proportional to the product of the frequency of stabilizing collisions and the lifetime of the autoionizing ion state. We assume, without further justification, that the frequency of stabilizing

collisions is independent of the ion state  $J\Sigma$ . At a given neutral gas density, the attachment can then be described through a phenomenological cross section of shape

$$\sigma_{\text{att}}(J\Sigma | n) \propto E(NJ\Sigma)^{3/2} B(J\Sigma | n) \delta(E - E(nJ\Sigma)). \quad (12)$$

It remains to determine the absolute values of the cross sections.

Shimamori and Hatano (1977) measured the thermal rate coefficient  $k_1$  for the resonant scattering process (6), and found a value  $k_1 = (4.8 \pm 0.6) \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$ . From this, the normalization of  $\sigma(J\Sigma | n)$  can be found by demanding that the relation

$$k_1 = \int f_{\text{M}}(\mathbf{v}) v \sigma_{\text{res}}(v) d\mathbf{v} / \int f_{\text{M}}(\mathbf{v}) d\mathbf{v} \quad (13)$$

be fulfilled. Here  $f_{\text{M}}(\mathbf{v})$  is the Maxwellian electron velocity distribution, and  $\sigma_{\text{res}}(v)$  is the total resonant cross section:

$$\sigma_{\text{res}}(v) = \sum_n g(n) \sum_{J\Sigma} \sigma(J\Sigma | n), \quad (14)$$

where  $g(n)$  is the statistical weight of the  $n$ th rotational state.

Hegerberg and Crompton (1983) measured the three-body attachment rate coefficient at 296 K, and found a value for  $k_{\text{att}}$  of  $2.24 \times 10^{-42} \text{ m}^6 \text{ s}^{-1}$ . Values at other temperatures were reported by Shimamori and Fessenden (1981). From this, the normalization of  $\sigma_{\text{att}}(J\Sigma | n)$  can be found by demanding that the relation

$$k_{\text{att}} = \int f_{\text{M}}(\mathbf{v}) v \bar{\sigma}_{\text{att}}(v) d\mathbf{v} / \int f_{\text{M}}(\mathbf{v}) d\mathbf{v} \quad (15)$$

be fulfilled, where

$$\bar{\sigma}_{\text{att}}(v) = \sum_n g(n) \sum_{J\Sigma} \sigma_{\text{att}}(J\Sigma | n). \quad (16)$$

Fig. 1 shows a collection of cross sections calculated as explained above. The resonant cross sections have been smoothed to simplify the illustration; if they are resolved, then more than 300 lines would appear.

### 3. Kinetic Theory

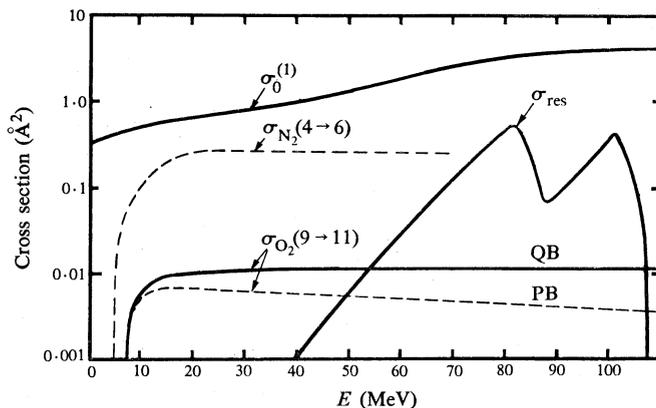
We assume that electron-electron collisions can be neglected, that the typical rate of change of the electron distribution  $f_e(\mathbf{r}, \mathbf{v}, t)$  is small compared with the rate of momentum transfer, and that the persistence of velocity in inelastic collisions contributes negligibly to the rate of momentum transfer.

The Boltzmann equation can then be reduced to a linear equation for the isotropic part  $f^{(0)}(\mathbf{r}, v, t)$  of  $f_e(\mathbf{r}, \mathbf{v}, t)$ , of the form (see e.g. Huxley and Crompton 1974)

$$\{\partial_t - (v^2/3\nu^{(1)})\nabla^2 + J_0\} f^{(0)}(\mathbf{r}, v, t) = 0, \quad (17)$$

where  $\nu^{(1)}$  is the collision frequency for momentum transfer, and  $J_0$  is the spherical component of rank zero of the full collision operator. The operator  $J_0$  is a sum of

operators representing elastic, inelastic and reactive collisions; explicit expressions for them will be given below.



**Fig. 1.** Collection of e-O<sub>2</sub> cross sections. Here  $\sigma_0^{(1)}$  is the non-resonant part of the momentum transfer cross section, and  $\sigma_{res}$  is the total resonant cross section [calculated with an  $E_0$  value of 100 meV (equation 7)];  $\sigma_{O_2}(9 \rightarrow 11)$  is a typical direct rotationally inelastic cross section, calculated in the quadrupole Born approximation (QB) as given by equation (5) and in the polarized Born approximation (PB). For comparison, a typical rotationally inelastic e-N<sub>2</sub> cross section is also shown.

### Separation of Variables

Following the method of Leemon and Kumar (1975), we separated the variables to solve equation (17). Insertion of the expression

$$f^{(0)}(\mathbf{r}, v, t) = R(\mathbf{r}) f(v) \theta(t), \quad (18)$$

where a summation over independent modes is implicitly understood, leads to the set of equations

$$(\nabla^2 + A^{-2})R(\mathbf{r}) = 0, \quad (19)$$

$$(d/dt + \lambda)\theta(t) = 0, \quad (20)$$

$$(v^2/3v^{(1)}A^2 + J_0)f(v) = \lambda f(v). \quad (21)$$

The separation constants  $A^{-2}$  and  $\lambda$  are determined by the eigenvalue equations (19) and (21) respectively. In equation (19) we impose the boundary condition  $R(\mathbf{r}_{wall}) = 0$ . Although not exact, this boundary condition gives negligible errors when the size of the system is large compared with the mean free path.

We are only interested in the asymptotic behaviour of the solution  $f^{(0)}(\mathbf{r}, v, t)$ , and are therefore looking for the smallest value of  $\lambda$ . Obviously this also means that we must select the smallest value of  $A^{-2}$ . For a cylindrical enclosure with diameter  $d$  and height  $h$  this value is

$$A_0^{-2} = (2\xi_0/d)^2 + (\pi/h)^2, \quad (22)$$

where  $\xi_0 = 2.405$  is the first zero of the Bessel function  $J_0$ . The quantity  $\Lambda_0$  is commonly designated 'the diffusion length'.

*Decay Time*  $\tau = \lambda^{-1}$

We split the operator  $J_0$  into a non-reactive (elastic plus inelastic) part and a reactive part,

$$J_0 = (J^{e1} + J^{in}) + J^R \equiv J^{(0)} + J^R, \quad (23)$$

and introduce an abbreviated notation for the diffusive loss term in equation (21),

$$v^2/3v^{(1)}\Lambda_0^2 \equiv D. \quad (24)$$

Equation (21) can then be written

$$J^{(0)} f(v) + (D + J^R)f(v) = \lambda f(v), \quad (25)$$

and by integration one finds formally, assuming that  $f(v)$  is normalized to 1,

$$\lambda \equiv \tau^{-1} = \int (D + J^R)f(v) dv. \quad (26)$$

To actually calculate  $\lambda$ , we must solve the eigenvalue equation (25). Before discussing how this can be done, we will give the explicit expressions for the collision operators.

### *Collision Operators*

Different forms of the collision operators are given in the literature (see e.g. Huxley and Crompton 1974). The elastic collision term can be written as

$$J^{e1} f(v) = -\frac{1}{2}v^{-2} \frac{d}{dv} \left\{ v^3 v_e(v) \left( f + \frac{kT}{mv} \frac{df}{dv} \right) \right\}. \quad (27)$$

Here  $v_e$  is the effective collision frequency for energy transfer,

$$v_e = 2(m_e/m_0)n_0 v \sigma_{e1}^{(1)}(v), \quad (28)$$

where  $m_e$  and  $m_0$  are the electron and neutral masses respectively,  $n_0$  is the neutral gas number density, and  $\sigma_{e1}^{(1)}(v)$  is the elastic collision contribution to the momentum transfer cross section.

The inelastic and superelastic collision terms can be merged together, using the principle of detailed balance, and written in the form

$$\begin{aligned} J_{ij}^{in} f(v) = & -(n_0^{(i)}/v)[v_+^2 \sigma_{ij}(v_+) \{f(v_+) - f(v) \exp(-\varepsilon_{ij}/kT)\} \\ & - v^2 \sigma_{ij}(v) \{f(v) - f(v_-) \exp(-\varepsilon_{ij}/kT)\}], \end{aligned} \quad (29)$$

where  $n_0^{(i)}$  is the density of neutrals in internal state  $i$ ,  $\varepsilon_{ij}$  is the energy loss in a transition  $i \rightarrow j$ ,  $\sigma_{ij}(v)$  is the cross section for this process, and  $v_+$  and  $v_-$  are speeds of an electron with initial speed  $v$ , after gain or loss respectively of an energy  $\varepsilon_{ij}$ .

The reactive collision operator is the purely algebraic operator

$$J^R f(v) = n_0 v \bar{\sigma}_{att}(v) f(v), \quad (30)$$

where  $\bar{\sigma}_{att}(v)$  is given by equation (16).

### Self-adjoint Operators

If a Boltzmann factor  $w(v) \propto \exp(-m_e v^2/2kT)$  is extracted from  $f(v)$ ,

$$f(v) = w(v) \phi(v), \quad (31)$$

then the collision operators regarded as operators on the function  $\phi(v)$  become self-adjoint (Robson 1976),

$$\int \psi(v) J_0(w(v) \phi(v)) dv = \int \phi(v) J_0(w(v) \psi(v)) dv. \quad (32)$$

It is therefore advantageous to introduce new collision operators

$$J^{el} \phi(v) \equiv w^{-1} J^{el}(w\phi) = \frac{1}{2} v_e v \frac{d\phi}{dv} - \frac{1}{2} \frac{kT}{mv^2} \frac{d}{dv} \left( v_e v^2 \frac{d\phi}{dv} \right), \quad (33)$$

$$\begin{aligned} J_{ij}^{in} \phi(v) &\equiv w^{-1} J_{ij}^{in}(w\phi) \\ &= -(n_0^{(i)}/v) [v_+^2 \sigma_{ij}(v_+) \{ \phi(v_+) - \phi(v) \} \exp(-\epsilon_{ij}/kT) \\ &\quad - v^2 \sigma_{ij}(v) \{ \phi(v) - \phi(v_-) \}], \end{aligned} \quad (34)$$

and thereby transform equations (25) and (26) to

$$(J^{(0)} + D + J^R) \phi(v) = \lambda \phi(v), \quad (35)$$

$$\lambda = \int w(v) (D + J^R) \phi(v) dv. \quad (36)$$

### Methods of Solution: Perturbation Expansion

If the loss terms  $D$  and  $J^R$  are small, the lowest eigenvalue  $\lambda_0$  and the associated eigenfunction  $\phi_0(v)$  may conveniently be found using a perturbation expansion around the equilibrium distribution  $\phi^{(0)} = 1$ . By inserting into equations (35) and (36) the formal expansions in an ordering parameter  $\eta$  (eventually to be put equal to one):

$$(D + J^R) \rightarrow \eta(D + J^R), \quad (37)$$

$$\phi_0 = 1 + \eta \phi^{(1)} + \eta^2 \phi^{(2)} + \dots, \quad (38)$$

$$\lambda_0 = \eta \lambda^{(1)} + \eta^2 \lambda^{(2)} + \dots, \quad (39)$$

thus gives to lowest order

$$\lambda^{(1)} = \int w(v) \{ D(v) + J^R(v) \} dv \quad (40)$$

and to higher orders, formally,

$$\lambda^{(i)} = (D + J^R, \phi^{(i-1)}), \quad (41)$$

$$\phi^{(i)} = (\lambda^{(i)} - J^{(0)})^{-1} \{ (D + J^R) \phi^{(i-1)} \}. \quad (42)$$

We have introduced here the scalar product

$$(\psi, \phi) \equiv \int w(v) \psi(v) \phi(v) dv \quad (43)$$

and an inverse operator  $(\lambda - J^{(0)})^{-1}$ , which is well-behaved when the following normalization condition is imposed:

$$(1, \phi^{(i)}) = 0. \quad (44)$$

#### *Methods of Solution: Rayleigh-Ritz Method*

If the loss terms are not small, the perturbation approach will fail, and some other method must be used. Robson (1976) used a nonlinear variational approach for the mathematically equivalent diffusion cooling problem. When high accuracies are needed, it is, however, necessary to use several variational parameters, and the use of nonlinear methods is then not feasible. We will therefore use a linear method.

The unknown function  $\phi_0$  is expanded in some set of real and linearly independent basis functions  $\psi_\alpha(v)$ :

$$\phi_0(v) = \sum_{\alpha=1}^N a_\alpha \psi_\alpha(v). \quad (45)$$

This expansion is inserted into equation (35), and scalar products are formed with other functions of the set  $\psi_\beta(v)$ , to get a set of  $N$  equations of the form

$$\sum_{\alpha=1}^N a_\alpha (\psi_\beta, (J^{(0)} + D + J^R - \lambda) \psi_\alpha) = 0 \quad (46)$$

or, introducing matrix elements  $S_{\beta\alpha} = (\psi_\beta, S\psi_\alpha)$ , to get equations of form

$$\sum_{\alpha=1}^N a_\alpha (J_{\beta\alpha}^{(0)} + D_{\beta\alpha} + J_{\beta\alpha}^R - \lambda \mathbf{1}_{\beta\alpha}) = 0, \quad (47)$$

where all matrices are symmetric, i.e.  $S_{\beta\alpha} = S_{\alpha\beta}$ .

The solution condition for equation (47), that

$$\det(J_{\beta\alpha}^{(0)} + D_{\beta\alpha} + J_{\beta\alpha}^R - \lambda \mathbf{1}_{\beta\alpha}) = 0, \quad (48)$$

determines  $N$  approximate values of  $\lambda$ , of which we select the smallest  $\bar{\lambda}_0$ . Due to the symmetry of the matrix equations, this smallest value  $\bar{\lambda}_0$  will be an upper bound to the exact eigenvalue  $\lambda_0$ .

After  $\bar{\lambda}_0$  has been determined from equation (48), the expansion coefficients  $a_\alpha$  are found by solving a set of  $N$  linear equations, composed of the normalization condition  $\sum_\alpha a_\alpha \mathbf{1}_{\alpha\alpha} = 1$  and of  $N-1$  of the equations (47).

#### 4. Numerical Methods and Results

We will solve equations (46)–(48) for the lowest eigenvalue  $\lambda_0$  and the associated eigenfunction  $\phi_0$ , using equations (27)–(30) for the collision operators and the cross sections given in Section 2. The diffusion length in the experiment of Hegerberg and Crompton (1983) was  $A_0 = 8.05$  mm, and this value is used throughout.

##### Representation of $\phi$

We choose to represent the function  $\phi(v)$ , which shows the relative deviation from a Maxwellian distribution, by its values in  $N$  equidistant points  $v_j = j\Delta v$ , in the range  $0 \leq v \leq 4(2kT/m_e)^{1/2}$ , using linear interpolation between the points. This is equivalent to the use of a hat-function basis (see e.g. Prenter 1975):

$$\psi_\alpha(v) = 1 - |v - v_\alpha|/\Delta v \quad \text{for } v_{\alpha-1} \leq v \leq v_{\alpha+1}, \quad (49a)$$

$$= 0 \quad \text{otherwise.} \quad (49b)$$

Typically, from 20 to 60 points were used.

##### Matrix Element Evaluation

The matrix elements  $S_{\alpha\beta}$ , where  $S$  symbolizes any of the relevant operators, are given by

$$S_{\alpha\beta} = (\psi_\alpha, S\psi_\beta) = \int_{v_{\alpha-1}}^{v_{\alpha+1}} w(v) \psi_\alpha(v) S\psi_\beta(v) dv. \quad (50)$$

The direct scattering matrix elements were calculated using the trapezoidal rule, while the resonant and attachment terms were calculated by summing over  $\delta$ -function contributions. The elastic collision operator (33) contains second order derivatives, and this is apparently inconsistent with the use of the basis set (49), which has discontinuous first order derivatives. The smoothness requirement can, however, be reduced by a partial integration, yielding

$$J_{\alpha\beta}^{el} = \frac{1}{2} \frac{kT}{m} \int w(v) v_e(v) \frac{d\psi_\alpha}{dv} \frac{d\psi_\beta}{dv} dv. \quad (51)$$

##### Perturbation Solution

The successive members of the perturbation series (38) are found by inserting for  $\phi^{(i)}$  the expansion

$$\phi^{(i)} = \sum_{\alpha=0}^{N-1} a_\alpha^{(i)} \psi_\alpha(v) \quad (52)$$

and solving for the expansion coefficients  $a_\alpha^{(i)}$  from an  $N \times N$  system of equations composed of the normalization condition (44) and  $N-1$  of the equations

$$\sum_{\alpha} a_\alpha^{(i)} (J_{\beta\alpha}^{(0)} - \mathbf{1}_{\beta\alpha} \lambda^{(i)}) = (\psi_\beta, (D + J^R) \phi^{(i-1)}). \quad (53)$$

The successive  $\lambda^{(i)}$  are calculated from the solution on level  $i-1$  from equation (41).

We used the perturbation expansion to calculate  $\phi^{(i)}$  to order  $i = 2$  and  $\lambda^{(i)}$  to order  $i = 3$ . If the corrections  $\lambda^{(2)}$  and  $\lambda^{(3)}$  were small (the criterion used was  $|\lambda^{(2)}/\lambda^{(1)}| < 0.1$  and  $|\lambda^{(3)}/\lambda^{(1)}| < 0.02$ ), then this was deemed satisfactory.

### Rayleigh–Ritz Solution

When the perturbation solution method failed, a full hat-function basis solution was performed, using a ‘shooting method’ outlined below. A trial eigenvalue  $\bar{\lambda}^{(0)}$  and two near-lying values  $\bar{\lambda}_{\pm}^{(0)}$  were chosen, and functions  $\phi_{\pm}$  calculated by solving a system of equations consisting of the normalization condition and  $N-1$  of the equations (47), with the  $\phi_{\pm}$  functions inserted. The last of the equations (47), number  $\gamma$  say, will now *not* be fulfilled, and insertion of the ‘solutions’  $\phi^{\pm}$  gives left-hand sides  $R^{\pm} \neq 0$ :

$$R^{\pm}(\lambda_{\pm}) = \sum_{\alpha=1}^N a_{\alpha}^{(\pm)}(J_{\gamma\alpha}^{(0)} + D_{\gamma\alpha} + J_{\gamma\alpha}^R - \lambda_{\pm} \mathbf{1}_{\gamma\alpha}) \neq 0. \quad (54)$$

From the values of  $R^{\pm}(\lambda_{\pm})$  a new trial eigenvalue  $\bar{\lambda}^{(1)}$  is obtained by linear extrapolation:

$$\bar{\lambda}^{(1)} = (\lambda_- R^+ - \lambda_+ R^-)/(R^+ - R^-). \quad (55)$$

Then new  $\bar{\lambda}_{\pm}$  are chosen, and the process is repeated until convergence, i.e. until a  $\lambda$  value is found which fulfils the whole system of equations. A first trial eigenvalue was estimated from the perturbation calculation. In all cases tested convergence was obtained after five iterations or less. The choice of ‘test equation  $\gamma$ ’ was found not to be of importance.

### Results

Fig. 2 shows the decay time constants  $\tau = 1/\lambda$  calculated using two different values for the resonance position parameter  $E_0$  (see equation 7). Also shown are the experimental values (circles) of Hegerberg and Crompton (1983) and the first order perturbation (i.e. Maxwellian distribution) values.

Fig. 3 shows the shapes of the eigenfunctions  $\phi(E)$ , calculated using  $E_0 = 86$  meV, for oxygen pressures of 1 and 2.5 kPa. The large rotational cross sections, associated with the resonances, force the distribution to have close to Maxwellian shape (i.e.  $\phi$  approximately constant) over most of the resonance region, and large deviations from Maxwellian shape occur below this region. An eigenfunction calculated for an equal mixture of  $O_2$  and  $N_2$  is also shown. The large direct rotational cross section in  $N_2$  (see Fig. 1) has the effect of decreasing the attachment cooling effect drastically.

## 5. Discussion

We feel that the main objective of this study, to explain the observed attachment cooling effects by a kinetic theory analysis, has been satisfactorily fulfilled.

Our calculations show clearly that the main reason for the appearance of the attachment cooling effect is the low value of the direct rotational excitation and de-excitation cross sections at energies below the attachment region. In the attachment region (50–100 meV), resonant rotational excitations ensure a nearly Maxwellian shape of the electron energy distribution.

In a recent paper, Koura (1982) has calculated the departure of the energy distribution from a Maxwellian shape *close to an attachment resonance*, and found it small. This is in agreement with the present findings. Koura's conclusion that this implies a vanishingly small attachment cooling effect, is however, untenable, and is due to his assumption of an infinite energy relaxation rate outside the resonance region.

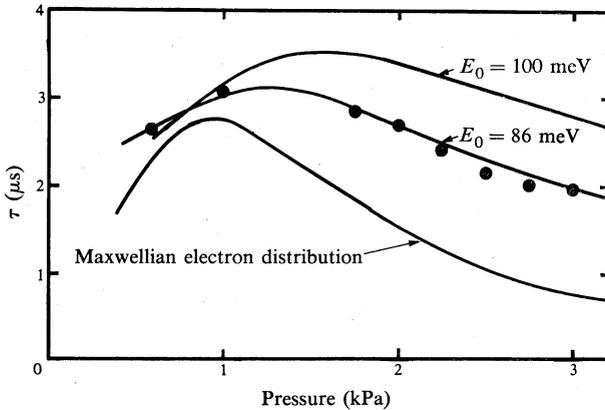


Fig. 2. Calculated and measured (circles) decay time constants for electrons in pure oxygen, as functions of the gas pressure.

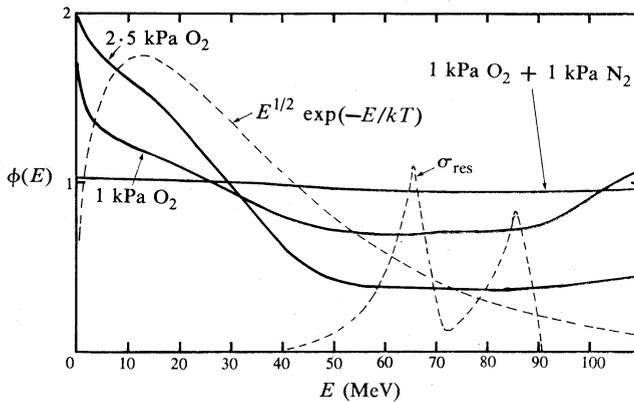


Fig. 3. Eigenfunctions  $\phi(E)$  for oxygen pressures of 1 and 2.5 kPa, and for an equal mixture of  $O_2$ - $N_2$ . An unperturbed energy distribution and the shape of the resonance cross section are also shown.

Agreement between calculated and experimentally observed decay times has been obtained by shifting the position of the attachment resonance, keeping other cross-section parameters constant. It should be pointed out, however, that the effects of shifting the resonance position downwards in energy and of increasing the non-resonant rotational excitation cross section are qualitatively the same. There are thus too many unknown parameters to perform any unique adjustment procedure. Furthermore, we have not taken into account attachment to van der Waals complexes, a process which may be of some importance also at room temperature according

to Shimamori and Fessenden (1981). Inclusion of this process would favour a shifting of the resonance position upwards in energy.

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