

# The coupling of electron thermalization and electron attachment in CCl<sub>4</sub>/Ar and CCl<sub>4</sub>/Ne mixtures

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The relaxation of a nonequilibrium distribution of electrons in a mixture of CCl<sub>4</sub> with either Ar or Ne is studied. In this paper, electron-CCl<sub>4</sub> and electron-inert gas elastic collisions, vibrationally inelastic collisions between electrons and CCl<sub>4</sub>, as well as the electron attachment reaction with CCl<sub>4</sub>, are included in the analysis. The time dependent electron energy distribution function is determined from the Boltzmann equation and the energy relaxation times are determined. The coupling of the thermalization process and the attachment process are discussed in detail. The results from the calculations are analyzed analogous to experimental studies, and the methodology of the experimental reduction of the data is studied. © 1998 American Institute of Physics. [S0021-9606(97)02546-4]

## I. INTRODUCTION

The study of the thermalization of electrons in atomic and molecular moderators is an important field of study and has a long history. Detailed reviews of the present status of the field that provide a bibliography of previous works were presented by Braglia<sup>1</sup> and by Shizgal *et al.*<sup>2</sup> The nature of the time dependent electron distribution function and average properties are important aspects of gas discharges,<sup>3</sup> plasma etching,<sup>4</sup> radiation chemistry and physics,<sup>5</sup> the development of gaseous insulators and switching devices,<sup>6</sup> the interpretation of electron swarm experiments,<sup>7</sup> environmental concerns and kinetic processes.<sup>8-10</sup> The main objective is to determine the time dependent electron distribution function and the nature of the steady distribution at long times, given some initial distribution.

The thermalization of energetic electrons in atomic and/or molecular moderators proceeds owing to collisions between the electrons and the constituents of the moderator assumed to be present in large excess. Electron-electron collisions are assumed not to occur and are not included in the theoretical analysis. A complete treatment would require the inclusion of elastic and inelastic collisions, and chemically reactive processes such as ionization and attachment. Recent papers reported continuing studies of electron thermalization in atomic moderators<sup>11-13</sup> in comparison with the earlier work by Shizgal and co-workers,<sup>14,15</sup> Mozumder<sup>16</sup> and Koura.<sup>17</sup> There have also been several papers on the thermalization of electrons in molecular moderators such as CH<sub>4</sub>,<sup>13,18</sup> SiH<sub>4</sub>,<sup>19</sup> H<sub>2</sub><sup>20</sup> and CH<sub>4</sub>/Ar mixtures.<sup>13</sup> In addition to these calculations, it is of considerable interest and importance to consider electron thermalization in electronegative gases for which it is important to include the attachment of

electrons. The attachment of electrons to electronegative gases in swarm type experiments is an important process in connection with gas discharges, plasma etching, radiation chemistry and physics.

The main objective of this paper is the study of the time evolution of the electron nonequilibrium distribution function from some initial distribution under the influence of elastic, and inelastic collisions of electrons with the ambient gases, and electron attachment to some electronegative gas. We consider a mixture of either Ar or Ne and CCl<sub>4</sub> so that the collision processes to be considered are elastic electron-inert gas and electron-CCl<sub>4</sub> collisions, and vibrationally inelastic electron-CCl<sub>4</sub> collisions and electron attachment to CCl<sub>4</sub>. The rate constant for the attachment of electrons to CCl<sub>4</sub> is very large. The inert gas moderators were chosen so as to have an example of a gas (Ar) with a momentum transfer cross section characterized by a Ramsauer-Townsend minimum and a second moderator (Ne) for which the momentum transfer cross section is nearly constant with energy. It is of considerable interest to contrast the relaxation behavior for these different moderators.

We consider a numerical solution of the time dependent Boltzmann equation for the electron energy distribution function and calculate the time variation of the electron number density and electron average energy. These quantities are characterized by time dependent energy relaxation rate coefficients and the attachment rate coefficients. Relaxation times are calculated in terms of the time required for the electron energy to reach within 10% of the steady average energy. The steady average energy of the electrons can be above the ambient temperature of the moderators because of the effect of attachment heating. This effect was discussed in the previous papers by Shizgal<sup>21-23</sup> except that in these works inelastic collisions were neglected.

The previous works by Shizgal showed that there can be a steady state distribution even though electron attachment

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involves a loss of electrons and a steady state would not be expected to occur. The basis for this theoretical work was the Fokker–Planck equation for elastic electron inert gas collisions and a term due to electron attachment. However, if there is a separation of relaxation times such that the energy thermalization occurs on a much faster time scale than attachment, then there can be a pseudo-steady distribution. The energy per particle attains a limiting value with the electron energy and the electron number density varying slowly with time on the time scale of the attachment process. In a recent paper, Kowari and Shizgal<sup>24</sup> extended this previous work to include vibrationally inelastic collisions as well. The main thrust of this previous paper was with regard to the existence of a steady distribution in the presence of the attachment process and a loss of electrons. However, the low energy portion of the attachment cross section used in this previous paper, the portion below 0.10 eV, does not coincide with the actual cross section for the system studied. The calculations are repeated in this paper for the correct cross section and the results are reinterpreted.

Warman and Sauer<sup>25</sup> reported an experimental technique to determine the energy relaxation rate coefficients and the relaxation times in pure inert gases and other moderators by following the reaction kinetics of electron attachment to CCl<sub>4</sub>. In this paper, we study the validity of the analysis used by Warman and Sauer to extract relaxation times from the electron kinetics associated with attachment. We compare the relaxation times extracted from the electron kinetics with those determined directly from the relaxation of the average energy. We also compare with the very recent measurements by Shimamori and Sunagawa.<sup>26</sup>

The formalism of the present paper follows the earlier papers on electron relaxation with the inclusion of vibrationally inelastic collisions but without electron attachment,<sup>18–20</sup> and the recent paper<sup>24</sup> that also includes electron attachment. In Section II, the Boltzmann equation for the electron energy distribution function is considered, and the numerical solution is discussed. The results and their discussion is presented in Section III. A reinterpretation of the work by Kowari and Shizgal<sup>24</sup> with regard to the existence of a steady electron distribution is presented in Section V.

## II. THE BOLTZMANN EQUATION

The theoretical method employed here follows closely that used previously,<sup>18–20</sup> which is based on the Boltzmann equation with collision terms for elastic and vibrationally inelastic collisions. The changes from this previous work due to the inclusion of the attachment to the molecular gas were discussed by Kowari and Shizgal.<sup>24</sup> Because there is no electric field applied to the system, it is reasonable to consider only the isotropic portion of the electron distribution function. We also assume that the electron distribution function is spatially homogeneous.

We write the Boltzmann equation with the collision term which explicitly includes electron attachment as well as elastic and inelastic collisions, as given by

$$\begin{aligned} \frac{\partial f}{\partial t} &= J(f) \\ &= J_{el}(f) + J_{in}(f) + J_a(f), \end{aligned} \quad (1)$$

where  $f = f(v, t)$ . In Eq. (1),  $J_{el}(f)$  and  $J_{in}(f)$  are the elastic and inelastic collision operators, respectively, and  $J_a(f)$  is the electron-attachment collision operator. Equation (1) no longer conserves the number of electrons because of electron attachment. We denote the mass of an electron by  $m$  and that of a molecule by  $M$ . For the small mass ratio  $m/M$ , the elastic collision operator is very well approximated by the differential Fokker–Planck operator<sup>14,15</sup>

$$J_{el} = \sum_{\gamma=1}^2 \frac{mN_{\gamma}}{M_{\gamma}v^2} \frac{\partial}{\partial v} \left[ v^4 \sigma_{\gamma}(v) \left( 1 + \frac{kT_b}{mv} \frac{\partial}{\partial v} \right) \right] f(v), \quad (2)$$

where  $N_{\gamma}$  is the number density of moderator  $\gamma$ ,  $k$  is the Boltzmann constant,  $T$  is the temperature of the moderator,  $v$  is the speed of an electron, and  $\sigma_{\gamma}(v)$  is the momentum transfer cross section for collisions of electrons with moderator  $\gamma$ . We take  $\gamma=1$  for CCl<sub>4</sub> and  $\gamma=2$  for either Ar or Ne.

The inelastic collision operator can be written as the sum over all the inelastic processes involved and can be cast in the form of a difference operator. The derivation of the inelastic collision operator is given in the Appendix of Ref. 18. A total inelastic cross section  $\sigma_{ij}(v)$  is given for an inelastic process between molecular states  $i$  and  $j$ . Then the inelastic collision operator is given as

$$J_{in} = N_1 v \sum_{i,j} \left[ n_i \frac{v'^2}{v^2} \sigma_{ij}(v') f(v') - n_i \sigma_{ij}(v) f(v) \right], \quad (3)$$

where  $v' = \sqrt{v^2 - 2\epsilon_{ij}/m}$ , and  $\epsilon_{ij} = \epsilon_j - \epsilon_i$  is the excitation energy transfer for internal molecular states  $i$  and  $j$ . The collision is inelastic if  $\epsilon_{ij} > 0$  and  $j > i$ , and it is super elastic if  $\epsilon_{ij} < 0$  and  $j < i$ . The population density of the molecular state is denoted by  $n_i$ , and  $\sum_i n_i = 1$ .

The electron attachment collision operator is  $J_a = -N_1 v \sigma_a(v) f(v)$ , where the electron attachment cross section for electron attachment to CCl<sub>4</sub> is  $\sigma_a(v)$ . The Boltzmann equation for the study of the relaxation of electrons is then,

$$\begin{aligned} \frac{\partial f}{\partial t} &= \sum_{\gamma=1}^2 \frac{mN_{\gamma}}{M_{\gamma}v^2} \frac{\partial}{\partial v} \left[ v^4 \sigma_{\gamma}(v) \left( 1 + \frac{kT_b}{mv} \frac{\partial}{\partial v} \right) \right] f(v) \\ &+ N_1 v \sum_{i,j} \left[ n_i \frac{v'^2}{v^2} \sigma_{ij}(v') f(v') - n_i \sigma_{ij}(v) f(v) \right] \\ &- N_1 v \sigma_a(v) f(v). \end{aligned} \quad (4)$$

In radiation physics and chemistry, it is customary to use an energy-dependent density  $\rho(\epsilon, t) \equiv 2\pi(2/m)^{3/2} \sqrt{\epsilon} f(v, t)$ , where  $\epsilon = mv^2/2$  and the track-length distribution (or incremental degradation spectrum)  $z(\epsilon, t) \equiv v\rho(\epsilon, t)$ . With the definitions of  $\rho(\epsilon, t)$  and  $z(\epsilon, t)$  in Eq. (4), we can obtain the expression for the time evolution of  $z(\epsilon, t)$ , that is,

$$\begin{aligned} \frac{1}{v} \frac{\partial z(\epsilon, t)}{\partial t} = & \sum_{\gamma=1}^2 \frac{2N_{\gamma}m}{M_{\gamma}} \frac{\partial}{\partial \epsilon} \left\{ \epsilon \sigma_{\gamma}(\epsilon) z(\epsilon, t) \right. \\ & \left. + \epsilon^2 \sigma_{\gamma}(\epsilon) kT_b \frac{\partial}{\partial \epsilon} \left[ \frac{z(\epsilon, t)}{\epsilon} \right] \right\} \\ & + N_1 \sum_{i,j} [n_i \sigma_{ij}(\epsilon') z(\epsilon', t) \\ & - n_i \sigma_{ij}(\epsilon) z(\epsilon, t)] - N_1 \sigma_a(\epsilon) z(\epsilon, t), \quad (5) \end{aligned}$$

where  $\epsilon' \equiv \frac{1}{2}mv'^2 = \epsilon + \epsilon_{ij}$ .

We consider the relaxation of electrons in a gas due to elastic and inelastic collisions. The inelastic collisions that may be important in the low energy regime are rotational and vibrational collisions. The present calculations do not explicitly involve rotationally inelastic collision processes because rotational excitation of such a highly symmetric molecule is expected to be small. The cross section for vibrational excitation from a vibrational state  $V$  to  $V'$  in the vibrational mode  $\nu$  is denoted by  $\sigma_{\nu}^{VV'}$  and the energy transfer by  $E_{\nu}^{VV'}$ . The population density of the vibrational state  $V$  in the vibrational mode  $\nu$  is denoted by  $n_{\nu}^V$ . It is necessary to replace the summation  $\sum_{i,j} \equiv \sum_i \sum_j$  with an explicit reference to the vibrational states, so that  $\sum_{i,j} = \sum_{\nu} \sum_{V} \sum_{V'}$ .

The Boltzmann equation with the differential operator for elastic collisions and the difference operator for vibrationally inelastic collisions is expressed by

$$\begin{aligned} \frac{1}{v} \frac{\partial z(\epsilon, t)}{\partial t} = & J(z) + \delta(\epsilon - \epsilon_0) \delta(t) \\ = & \sum_{\gamma=1}^2 \frac{2N_{\gamma}m}{M_{\gamma}} \left\{ \left[ \frac{\partial}{\partial \epsilon} \epsilon \sigma_{\gamma}(\epsilon) z \right. \right. \\ & \left. \left. + \frac{\partial}{\partial \epsilon} (\epsilon^2 \sigma_{\gamma}(\epsilon)) kT_b \frac{\partial}{\partial \epsilon} \left( \frac{z}{\epsilon} \right) \right. \right. \\ & \left. \left. + \epsilon^2 \sigma_{\gamma}(\epsilon) kT_b \frac{\partial^2}{\partial \epsilon^2} \left( \frac{z}{\epsilon} \right) \right] \right\} \\ & + N_1 \left[ \sum_{\nu} \sum_{V} n_{\nu}^V \sum_{V'} \sigma_{\nu}^{VV'} (\epsilon + \epsilon_{\nu}^{VV'}) z(\epsilon \right. \\ & \left. + \epsilon_{\nu}^{VV'}, t) - \sum_{\nu} \sum_{V} n_{\nu}^V \sum_{V'} \sigma_{\nu}^{VV'} (\epsilon) z(\epsilon, t) \right] \\ & - N_1 \sigma_a(\epsilon) z(\epsilon, t) + \delta(\epsilon - \epsilon_0) \delta(t). \quad (6) \end{aligned}$$

In Eq. (6), the delta functions on the right-hand side show explicitly the initial electron distribution as a delta function at energy  $\epsilon_0$ . The electron number density and energy are given by

$$n(t) = \int f(v, t) dv, \quad (7)$$

$$E_{total}(t) = \int f(v, t) \frac{mv^2}{2} dv, \quad (8)$$

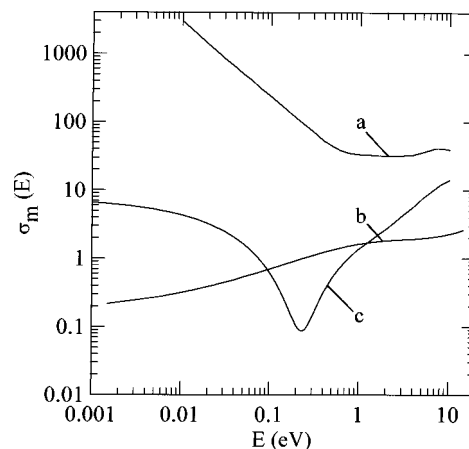


FIG. 1. Energy dependence of momentum transfer cross sections.  $\sigma_m(E)$  is in units of  $10^{-16} \text{ cm}^2$ . (a)  $\text{CCl}_4$ , (b) neon and (c) argon.

respectively. The average electron energy per electron is then

$$E(t) = \frac{E_{total}}{n(t)}. \quad (9)$$

### III. CROSS SECTION DATA SET

The momentum transfer cross sections for elastic collisions with either Ar, Ne or  $\text{CCl}_4$  are shown in Fig. 1. The momentum transfer cross section for Ar used in the present calculations is constructed as follows. We obtain the data below 1 eV by using the modified effective range theory (MERT) procedure given by Haddad and O'Malley.<sup>27</sup> We calculate the MERT procedure for the energy range of 0 eV and 0.32 eV with the MERT parameters<sup>27</sup> for the upper limit of 0.5 eV and for the energy range of 0.32 eV and 1 eV with that for the upper limit of 1 eV. We use Table I of Ref. 28 between 1 eV and 4 eV and Table II of Ref. 29 above 4 eV.

TABLE I. Electron relaxation times in  $\mu\text{s Torr}$ .

$X_{\text{CCl}_4}$	$p\tau_{1,1}^a$	$p\tau_{1,1}^b$	$E(\infty)/E_{th}$
1.0(-7)	5091	5416	1.445
3.0(-7)	2942	4219	1.741
5.0(-7)	2171	3141	1.982
1.0(-6)	1404	1769	2.344
3.0(-6)	683.5	812.7	2.735
5.0(-6)	481.4	572.6	2.903
8.0(-6)	343.6	416.7	3.055
1.0(-5)	291.1	354.5	3.127
2.0(-5)	169.1	220.5	3.357
3.0(-5)	120.6	164.6	3.495
4.0(-5)	94.37	133.3	3.597
5.0(-5)	77.48	112.2	3.683
6.0(-5)	66.01	96.29	3.760
7.0(-5)	57.44	84.03	3.827
8.0(-5)	50.84	73.49	3.896
1.0(-4)	41.30	59.33	3.982
3.0(-4)	14.52	...	4.830
5.0(-4)	8.90	...	5.219
1.0(-3)	4.59	...	5.829

<sup>a</sup> $\text{CCl}_4$  in Ar without attachment.

<sup>b</sup> $\text{CCl}_4$  in Ar with attachment.  $p\tau_{1,1} = 5570 \mu\text{s Torr}$  for pure Ar; Ref. 14.

TABLE II. Electron relaxation times in  $\mu\text{s Torr}$ .

$X_{\text{CCl}_4}$	$p\tau_{1.1}^a$	$p\tau_{1.1}^b$	$E(\infty)/E_{th}$
1.0(-8)	2944	...	...
3.0(-8)	2842	...	...
5.0(-8)	2748	...	...
6.0(-8)	2704	...	1.087
8.0(-8)	2620	2339	1.104
1.0(-7)	2543	2083	1.134
2.0(-7)	2224	1802	1.200
3.0(-7)	1988	1583	1.270
4.0(-7)	1804	1311	1.323
6.0(-7)	1537	1035	1.411
8.0(-7)	1349	873.6	1.476
1.0(-6)	1209	769.2	1.526
3.0(-6)	638.1	448.2	1.812
1.0(-5)	271.0	248.2	2.187
3.0(-5)	112.8	126.9	2.762
1.0(-4)	39.67	52.44	3.475
3.0(-4)	14.30	13.12	4.502

<sup>a</sup>CCl<sub>4</sub> in Ne without attachment.

<sup>b</sup>CCl<sub>4</sub> in Ne with attachment.  $p\tau_{1.1}=2960 \mu\text{s Torr}$  for pure Ne; Ref. 14.

The momentum transfer cross section of Ne is taken from O'Malley and Crompton,<sup>30</sup> and the one for CCl<sub>4</sub> is from Hayashi.<sup>31</sup> The cross section for Ar and CCl<sub>4</sub> are characterized by Ramsauer-Townsend minima whereas the one for Ne is not.

CCl<sub>4</sub> belongs to  $T_d$  symmetry and has nine normal modes of which only four, denoted by  $\nu_1-\nu_4$ , are distinguishable because of degeneracy. The excitation energies from the vibrational ground state to the first excited vibrational state for each mode are 0.0569 eV, 0.0269 eV, 0.0962 eV, and 0.0389 eV, respectively.<sup>34</sup> The four vibrationally inelastic cross sections characterized by these threshold energies are shown in Fig. 2. Because the population densities of some of the highly excited vibrational states in each normal mode are not negligible (for example,  $n_{\nu_1}^1$  is 9.8 percent,  $n_{\nu_2}^1$  is 22.8 percent,  $n_{\nu_3}^1$  is 2.4 percent and  $n_{\nu_4}^1$  is 17.3 per-

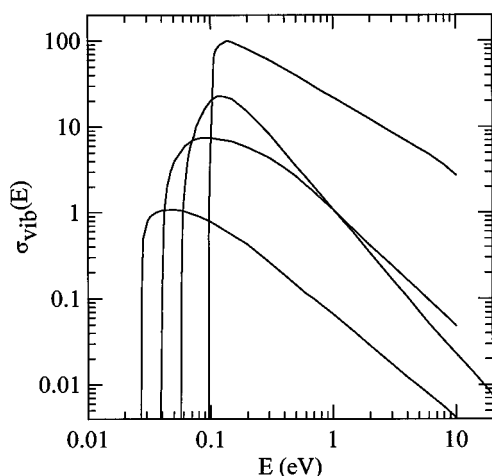


FIG. 2. Energy dependence of the four vibrationally inelastic cross sections for electron-CCl<sub>4</sub> collisions. The threshold energies are 0.0269, 0.0389, 0.0569 and 0.0962 eV, respectively.

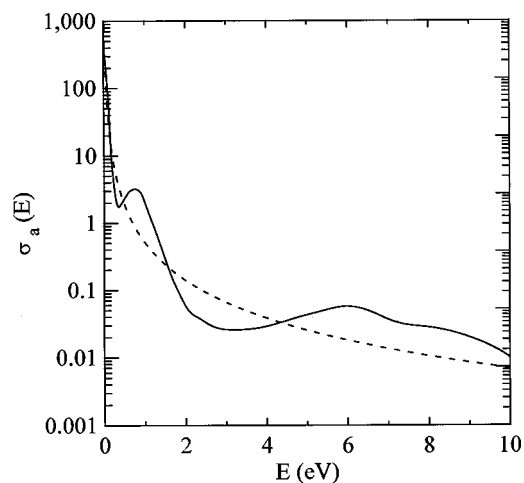


FIG. 3. The solid line is the energy dependence of the electron-CCl<sub>4</sub> attachment cross section. The dashed line is the approximate power law cross section given by  $\sigma_a(E)=0.5178E^{-1.88}$ , with  $E$  in eV and  $\sigma_a$  in  $10^{-16} \text{ cm}^2$ .

cent), we take account of the transitions from up to  $V=3, 8, 2$ , and  $5$  for  $\nu_1-\nu_4$ , respectively; all with  $\Delta V=1$ . In order to take account of these transitions, we need cross sections from vibrationally excited states to the upper states of those states in each vibrational mode. However, available cross sections on vibrationally inelastic collisions for both modes are those for  $V=0\rightarrow 1$ , and the scaling laws Ref. 32 to construct vibrationally inelastic cross sections for vibrationally excited states are not applicable to the present case. Therefore, we assume the cross sections with the transition from  $V$  to  $V+1$  where  $V\geq 1$  for the four normal modes are the same as those from  $V=0$  to  $1$ . The cross sections with the transitions from  $V+1$  to  $V$  for the four normal modes are obtained using the relation for microscopic reversibility,  $\epsilon\sigma_{ij}(\epsilon)=(\epsilon-\epsilon_{ij})\sigma_{ji}(\epsilon-\epsilon_{ij})$ .

We use Hayashi's electron attachment cross section<sup>31</sup> for electron attachment to CCl<sub>4</sub>. Hayashi's electron attachment cross section is consistent with that of Chutjian and Alajajian<sup>33</sup> at low energies and we use the analytical expression of Chutjian and Alajajian

$$\sigma(\epsilon) = 545 \left\{ \frac{0.117}{\sqrt{\epsilon}} \exp \left[ - \left( \frac{\epsilon}{0.005} \right)^2 \right] + \exp \left( - \frac{\epsilon}{0.056} \right) \right\} \quad (10)$$

below  $0.1 \text{ eV}$ .<sup>33</sup> The thermal attachment rate coefficient at  $300 \text{ K}$  given by  $K_{th}=2.94\times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  is in excellent accord with the value of  $2.96\times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  at  $296 \text{ K}$  reported by Blaustein and Christophorou<sup>35</sup> and in good agreement with the value of  $3.5\times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  at  $(298\pm 3 \text{ K})$  by Shimamori and Sinagawa.<sup>26</sup> The attachment cross section is shown in Fig. 3. The dashed curve in the figure is the power law fit to the high energy portion of the attachment cross section. In the previous papers,<sup>22-24</sup> the analytic expression in Eq. (10) was incorrectly reported with power of  $\epsilon$  as  $\frac{1}{2}$  rather than as  $-\frac{1}{2}$ . In the first two papers cited, this was just a typographical error and the calculations were reported for

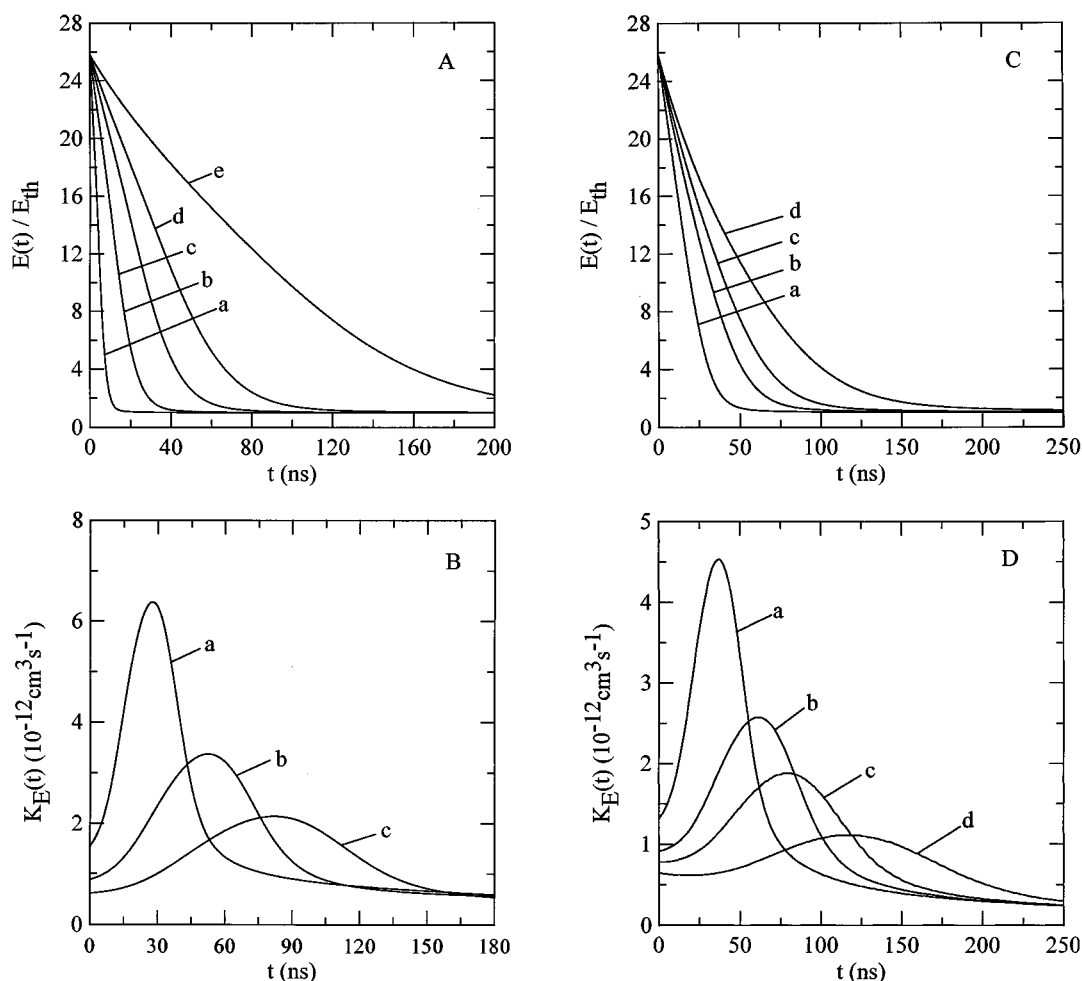


FIG. 4. Electron relaxation in  $\text{CCl}_4/\text{Ar}$  and  $\text{CCl}_4/\text{Ne}$  mixtures without attachment. (A) Time variation of the average energy in  $\text{CCl}_4/\text{Ar}$  for different  $\text{CCl}_4$  mole fractions equal to (a)  $3 \times 10^{-4}$ , (b)  $10^{-4}$ , (c)  $5 \times 10^{-5}$ , (d)  $3 \times 10^{-5}$  and (e)  $10^{-5}$ . (B) Time variation of the energy relaxation rate coefficient in  $\text{CCl}_4/\text{Ar}$  for different  $\text{CCl}_4$  mole fractions equal to (a)  $10^{-4}$ , (b)  $5 \times 10^{-5}$  and (c)  $3 \times 10^{-5}$ . (C) Time variation of the average energy in  $\text{CCl}_4/\text{Ne}$  for different  $\text{CCl}_4$  mole fractions equal to (a)  $10^{-4}$ , (b)  $6 \times 10^{-5}$ , (c)  $3 \times 10^{-5}$  and (d)  $10^{-5}$ . (D) Time variation of the energy relaxation rate coefficient in  $\text{CCl}_4/\text{Ne}$  for different  $\text{CCl}_4$  mole fractions equal to (a)  $10^{-4}$ , (b)  $6 \times 10^{-5}$ , (c)  $3 \times 10^{-5}$  and (d)  $10^{-5}$ .

the correct cross section. In the most recent work by Kowari and Shizgal,<sup>24</sup> a different attachment cross section was used as discussed in detail in Section V.

#### IV. CALCULATIONS AND RESULTS

The Boltzmann equation for the specified cross sections is solved with a finite difference technique for both energy and time as discussed in previous papers.<sup>19,20</sup> The initial distribution function is a delta function at 1.0 eV. We use a temperature of 300 K for the background gases  $\text{CCl}_4$  and either Ar or Ne and the total number density is  $2.69 \times 10^{19} \text{ cm}^{-3}$ . At each time step we solve the finite difference equation with the successive over-relaxation method.<sup>36</sup>

In theoretical calculations, unlike in the experiments, it is possible to study the effect of the omission or inclusion of different cross sections to understand the role of different processes. In Fig. 4, we show the relaxation of the electron energy in  $\text{CCl}_4/\text{Ar}$  [Fig. 4(A)] and  $\text{CCl}_4/\text{Ne}$  [Fig. 4(C)] in the absence of the electron attachment process. The different

curves are for different  $\text{CCl}_4$  mole fractions. The electron energy decreases with time and attains the average energy  $E_{th} = \frac{3}{2}kT_b$  which for a moderator temperature at 300 K is 0.0388 eV, so that  $E(0)/E_{th} = 25.79$ . Figure 4(B) and 4(D) show the time variation of the energy relaxation rate coefficient defined by,

$$K_E(t) = - \left[ \frac{E(t)}{E_{th}} - 1 \right]^{-1} \frac{d E(t)}{dt E_{th}}. \quad (11)$$

The behavior of the electron energy relaxation with Ar or Ne as moderators is similar. The rapid increase in the rate of energy relaxation with the addition of  $\text{CCl}_4$  is due to the inclusion of the vibrationally inelastic collisions. If  $K_E$  in Eq. (11) is assumed to be constant, the integration of Eq. (11) leads to an exponential decay of the average energy, that is,

$$\left( \frac{E(t)}{E_{th}} - \frac{E(\infty)}{E_{th}} \right) = \left( \frac{E(0)}{E_{th}} - \frac{E(\infty)}{E_{th}} \right) e^{-K_E t}, \quad (12)$$

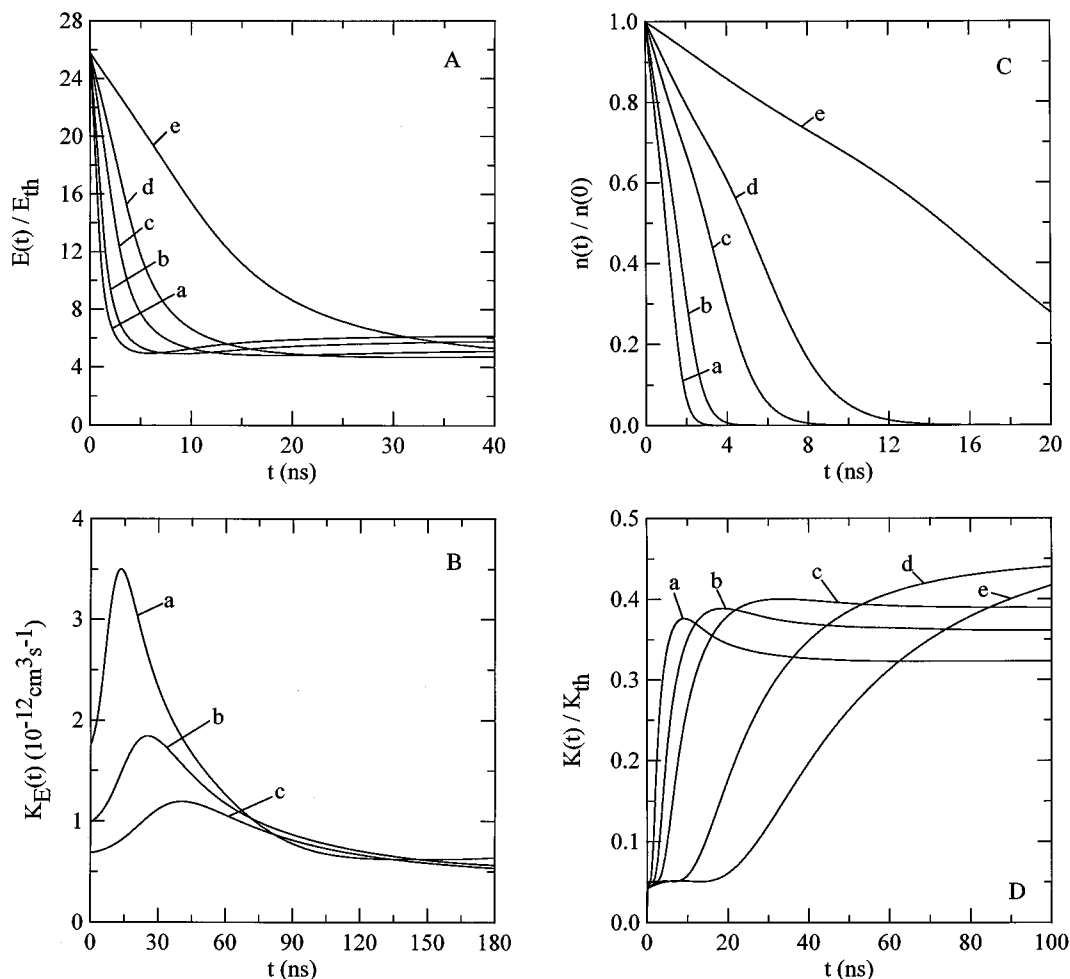


FIG. 5. Electron relaxation in  $\text{CCl}_4/\text{Ar}$  with attachment. (A) Time variation of the average energy for different  $\text{CCl}_4$  mole fractions equal to (a)  $1.5 \times 10^{-3}$ , (b)  $10^{-3}$ , (c)  $5 \times 10^{-4}$ , (d)  $3 \times 10^{-4}$  and (e)  $10^{-4}$ . (B) Time variation of the energy relaxation coefficient for different  $\text{CCl}_4$  mole fractions equal to (a)  $10^{-4}$ , (b)  $3 \times 10^{-5}$  and (c)  $5 \times 10^{-5}$ . (C) Time variation of the number density for different  $\text{CCl}_4$  mole fractions equal to (a)  $1.5 \times 10^{-3}$ , (b)  $10^{-3}$ , (c)  $5 \times 10^{-4}$ , (d)  $3 \times 10^{-4}$  and (e)  $10^{-4}$ . (D) Time variation of the attachment rate coefficient for different  $\text{CCl}_4$  mole fractions equal to (a)  $10^{-3}$ , (b)  $5 \times 10^{-4}$ , (c)  $3 \times 10^{-4}$ , (d)  $10^{-4}$  and (e)  $5 \times 10^{-5}$ .

where  $E(\infty)/E_{th}=1$  if there is no attachment, and  $E(\infty)/E_{th} \geq 1$  with attachment heating as discussed later. The time variation of the energy rate coefficients is indicative of the fact that the energy relaxation is not a pure exponential decay. This is anticipated since for this linear problem, the time dependence can be expressed as a sum of exponential terms with each term characterized by an eigenvalue of the collision operator. This was the approach adopted with analysis that did not include the vibrationally inelastic collisions.<sup>21-23</sup> With the inclusion of inelastic collisions, the eigenvalue spectrum of the operator should be modified by the occurrence of very large eigenvalues that characterize the time scale for vibrationally inelastic collisions. Semilogarithmic plots of  $E(t)/E_{th}$  versus time that are not shown here suggest that the energy relaxation could be fitted to a sum of three exponential terms. It would be of considerable interest to extract and compare from both the theoretical and experimental data, the two or three dominant exponential terms.<sup>20,37</sup> If Eq. (12) was valid, then there is a simple relationship between  $K_E$  and  $p\tau_{1,1}$  given by<sup>25</sup>

$$p\tau_{1,1} = \frac{2.303}{NK_E} \left[ 1 + \log \left( \frac{E(0)}{E(\infty)} - 1 \right) \right], \quad (13)$$

where  $N = 3.22 \times 10^{16} \text{ cm}^{-3}$  is the density at 1 Torr and 300 K.

In Figs. 5 and 6, we show the time variation of the electron energy and density with the inclusion of the attachment process for  $\text{CCl}_4/\text{Ar}$  and  $\text{CCl}_4/\text{Ne}$  mixtures, respectively. The main difference with the behavior without attachment is that the electron number density decays rapidly and the average electron energy attains a steady value above the thermal energy of the moderators. This is the attachment heating effect. The effect increases with increasing concentration of  $\text{CCl}_4$  as shown in Fig. 7 and in Tables I and II.

In Figs. 5(B) and 6(B), we also show the energy relaxation rate coefficients, and in Figs. 5(D) and 6(D) the time dependence of the attachment rate coefficient defined by

$$K(t) = -\frac{1}{n} \frac{dn}{dt}. \quad (14)$$

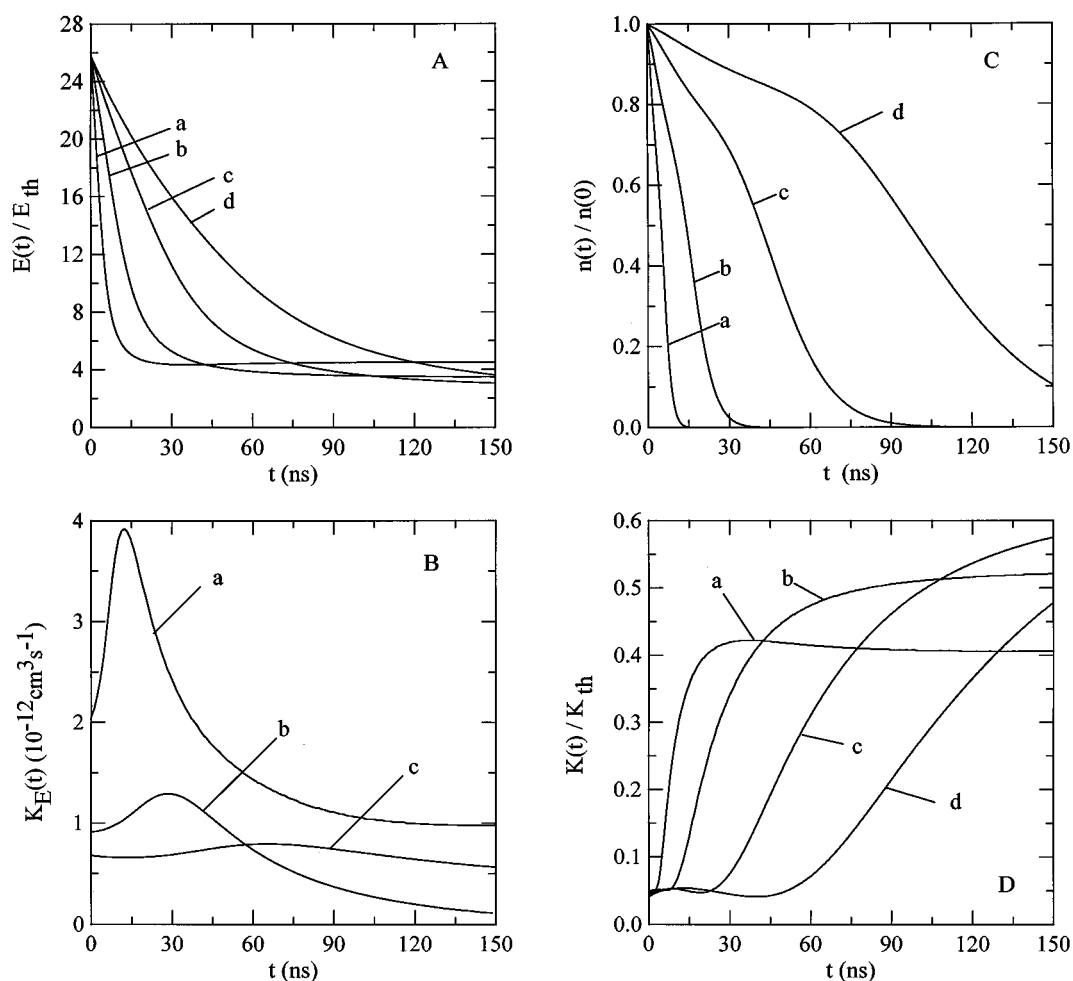


FIG. 6. Electron relaxation in  $\text{CCl}_4/\text{Ne}$  with attachment. (A) Time variation of the average energy for different  $\text{CCl}_4$  mole fractions equal to (a)  $10^{-5}$ , (b)  $3 \times 10^{-5}$ , (c)  $10^{-4}$  and (d)  $3 \times 10^{-4}$ . (B) Time variation of the energy relaxation coefficient for different  $\text{CCl}_4$  mole fractions equal to (a)  $10^{-4}$ , (b)  $3 \times 10^{-5}$  and (c)  $10^{-5}$ . (C) Time variation of the number density for different  $\text{CCl}_4$  mole fractions equal to (a)  $3 \times 10^{-4}$ , (b)  $10^{-4}$ , (c)  $3 \times 10^{-5}$  and (d)  $10^{-5}$ . (D) Time variation of the attachment rate coefficient for different  $\text{CCl}_4$  mole fractions equal to (a)  $5 \times 10^{-4}$ , (b)  $10^{-4}$ , (c)  $5 \times 10^{-5}$  and (d)  $10^{-5}$ .

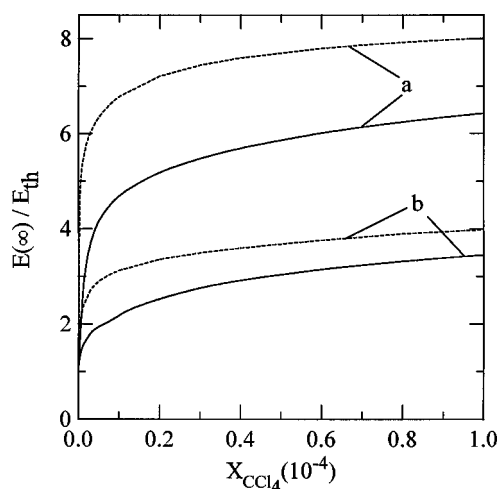


FIG. 7. The attachment heating effect for electrons in  $\text{CCl}_4/\text{Ar}$  (dashed curves) and  $\text{CCl}_4/\text{Ne}$  (solid curves) mixtures. (a) without inelastic collisions, (b) with inelastic collisions.

The energy relaxation rate coefficients shown in Figs. 5(B) and 6(B) vary with time, indicative of a multi-exponential decay as was the case without attachment. The inclusion of attachment appears to have reduced the  $K_E$  values by roughly a factor of 2 in the case of Ar as moderator. The reduction in  $K_E$  with Ne as the moderator is somewhat less. The attachment rate coefficients increase rapidly and attain a steady value which is significantly less than the thermal values at 300 K. We calculate the steady electron distribution functions for different  $\text{CCl}_4$  concentrations for  $\text{CCl}_4/\text{Ar}$  and  $\text{CCl}_4/\text{Ne}$  mixtures. The distributions are presumably strongly perturbed from Maxwellian as seen in the  $E(\infty)/E_{th}$  values greater than 1 shown in Fig. 7. This nonequilibrium effect appears to be somewhat larger for Ar than for Ne, perhaps due to the Ramsauer–Townsend minimum in the momentum transfer cross section for Ar.

The main quantity of interest, in particular with the comparison with experiment, is the relaxation time for the energy relaxation. Since the relaxation of the average energy (and the number density) is not a pure exponential, there is no

unique definition of a relaxation time. It has become customary to define a relaxation time,  $\tau_{1,1}$ , as the time required to approach within 10% of the steady energy per particle,  $E(\infty)$ . The variation of this thermalization time, with and without attachment, versus  $\text{CCl}_4$  mole fraction is shown in Tables I and II. Also shown in the tables is the steady electron energy relative to the thermal energy. This illustrates the attachment heating effect with increasing  $\text{CCl}_4$  concentration. The results in Table I show that the thermalization time decreases rapidly with an increase in the  $\text{CCl}_4$  concentration. This is due primarily to the increased energy loss from vibrationally inelastic collisions. The electron attachment process increases the relaxation time at all concentrations shown in Table I. This is consistent with the decrease in the  $K_E$  values shown previously in Figs. 4(B) and 5(B). With increasing  $\text{CCl}_4$  concentration, the nonequilibrium attachment heating effect increases strongly as seen from the rapid increase in  $E(\infty)/E_{th}$ . The asterisks in the table indicate that a relaxation time could not be defined owing to a minimum in the time variation of  $E(t)/E_{th}$ .

The results for Ar as moderator in Table II are similar in some respects and different in others. The relaxation times decrease with increasing  $\text{CCl}_4$  concentration but the inclusion of the attachment process decreases the relaxation times for small concentrations and increases the relaxation time for the larger concentrations. It is important to note that the results for very small concentrations that are shown in Table II were not included in Table I. The determination of the final steady electron energy for the smallest concentrations requires considerable computation and their determination is difficult. We did not obtain reliable results for Ar at the smallest concentrations ( $X_{\text{CCl}_4} \approx 10^{-8}$ ), and for Ne only the relaxation times without attachment could be obtained. In this case, the final energy is the thermal energy,  $E(\infty)/E_{th}=1$ , and the time integrations do not have to be carried out to a steady state. The asterisks in Table II also indicate that reliable results could not be obtained for the entries at the lowest concentrations. In Fig. 7, the solid curves are for  $\text{CCl}_4/\text{Ne}$  and the dashed curves are for  $\text{CCl}_4/\text{Ar}$ . The curves labelled (a) correspond to the heating in the absence of inelastic collisions whereas the curves labelled (b) are for the situation with inelastic collisions. The effect of the inelastic collisions to cool the gas is clear. The variation of  $E(\infty)/E_{th}$  with  $X_{\text{CCl}_4}$  is not linear except for perhaps the smallest concentrations.

In Fig. 8, we show the results of calculations of  $\tau_{1,1}$  for  $\text{CCl}_4/\text{Ne}$  mixtures for very small  $\text{CCl}_4$  concentrations without the attachment process. These  $p\tau_{1,1}$  values are also included in Table II. The dots show the results of the calculations at five  $\text{CCl}_4$  concentrations. The solid line through the points is a linear fit, the slope of which gives  $\tau_{1,1}$  for  $\text{CCl}_4$  without attachment. We find from the slope that  $p\tau_{1,1} = 1.68 \times 10^{-3} \mu\text{s Torr}$  without attachment. The intercept in the figure provides the relaxation time for pure Ne and is  $2994 \mu\text{s Torr}$ , in agreement with the previous result of  $2960 \mu\text{s Torr}$ .<sup>14</sup> We could not carry out similar calculations with attachment for these small concentrations as the determina-

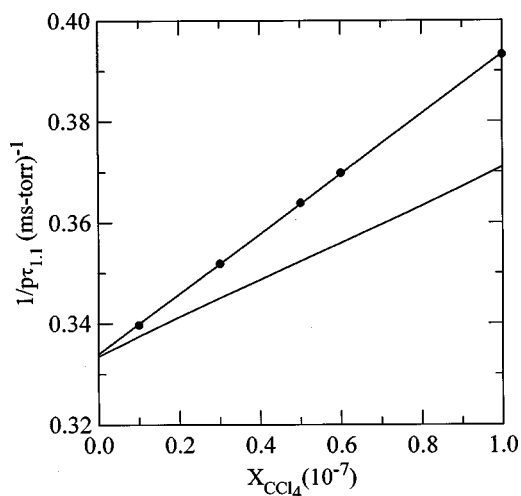


FIG. 8. The variation of  $1/p\tau_{1,1}$  versus mole fraction  $\text{CCl}_4$  in Ne. The solid symbols are the results of the calculation and the solid line through the points is a linear fit. The line below without symbols is the result without inelastic collisions. Note that the mole fraction of  $\text{CCl}_4$  is extremely small.

tion of  $E(\infty)/E_{th} \geq 1$  is inaccurate and requires very long time integrations.

The concentration dependence of the relaxation times for both  $\text{CCl}_4/\text{Ar}$  and  $\text{CCl}_4/\text{Ne}$  for much larger concentrations is shown in Fig. 9. The curve labelled (a) is with inelastics and without attachment. The curves labelled (b) include both inelastics and attachment. The lower solid curve labelled (c) does not include inelastic collisions but does include attachment. This illustrates the lengthening of the relaxation time due to the attachment process at relatively large  $\text{CCl}_4$  concentrations. Notice that for Ar as moderator the curve labelled (b) lies above the curve labelled (a) at the lowest concentrations. This shows the decrease in the relaxation time due to attachment as previously discussed in connection with the results in Table II.

In Fig. 10, we carry out a calculation of the energy relaxation rate coefficient assumed independent of time from the time variation of the electron density as previously done by Warman and Sauer<sup>25</sup> in the interpretation of their experimental results. Their work is based on the power law approximation of the attachment cross section versus energy, that is,

$$\sigma(E) = \frac{\sigma_0}{E^s} \quad (15)$$

for which the equilibrium attachment rate coefficient varies with temperature as given by

$$K(T(t)) = \sqrt{\frac{2}{\pi m}} \sigma_0 [kT(t)]^{-s+1/2} \Gamma(2-s), \quad (16)$$

where  $\Gamma(x)$  is the gamma function. If one sets,  $E(t) = \frac{3}{2}kT(t)$  and  $E_{th} = \frac{3}{2}kT_b(0)$ , then this gives the relation between the time dependent attachment rate coefficient and the time dependent average electron energy, that is,

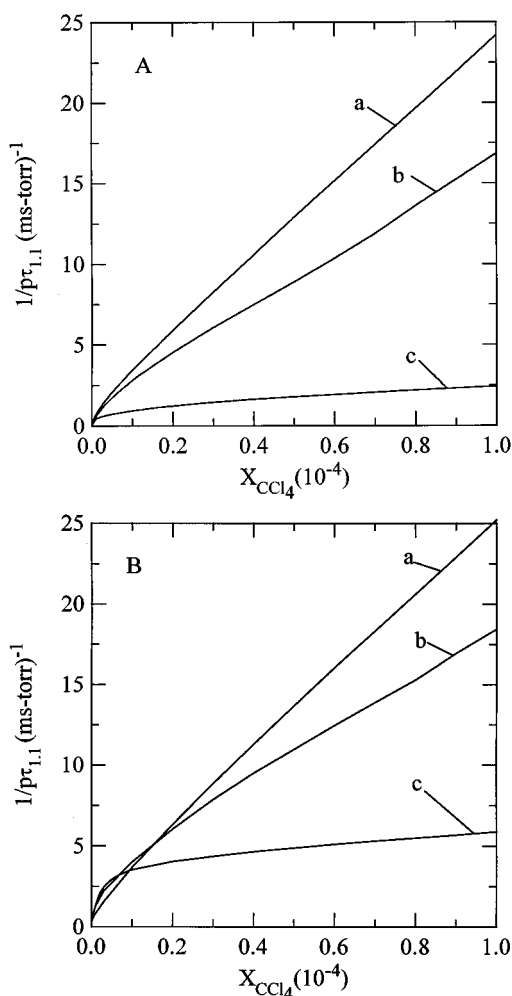


FIG. 9. The variation of  $1/p\tau_{1,1}$  versus mole fraction  $\text{CCl}_4$ . (a) with inelastic collisions and without attachment, (b) with inelastic collisions and with attachment, (c) without inelastic collisions and with attachment. (A)  $\text{CCl}_4/\text{Ar}$  mixtures, (B)  $\text{CCl}_4/\text{Ne}$  mixtures.

$$\frac{K(t)}{K_{th}} = \left[ \frac{E(t)}{E_{th}} \right]^{-p}, \quad (17)$$

where  $p = s - \frac{1}{2}$ . Equation (16) assumes that the electron velocity distribution function remains a Maxwellian with a time dependent temperature. This concept was used previously by Mozumder<sup>16</sup> in his study of electron thermalization and a similar approach was also considered in the treatment of hot atom reactions.<sup>38-41</sup> If Eq. (17) is combined with Eq. (12), we get that

$$\ln \left[ \left( \frac{K(t)}{K_{th}} \right)^{-1/p} - 1 \right] = -K_E t. \quad (18)$$

Warman and Sauer determined values of  $K_E$  from the kinetics of the attachment process and Eq. (18). We have used the calculated  $n(t)$  and  $K(t)$  data, and extracted  $K_E$  values by fitting the results to Eq. (18). This is shown in Fig. 10(A) and 10(C) for  $\text{CCl}_4/\text{Ar}$  and  $\text{CCl}_4/\text{Ne}$  mixtures, respectively. We have chosen to fit the curves between (approximately) the times for which  $n(t)/n(0) = 0.8$  and  $n(t)/n(0) = 0.05$ . The

dashed lines in Figs. 10(A) and 10(C) are the linear fits to the calculated  $K(t)$  curves and the slopes are related to the  $K_E$  coefficients as given by Eq. (18). It is important to emphasize that Eq. (17) is valid for a power law attachment cross section, an electron distribution that remains Maxwellian and time independent  $K_E$  coefficients. From the results presented here these assumptions are not rigorously valid.

The variation of the  $K_E$  coefficients with  $\text{CCl}_4$  concentration determined from the slopes of the fits in Figs. 10(A) and 10(C) is shown in Figs. 10(B) and 10(D) for  $\text{CCl}_4/\text{Ar}$  and  $\text{CCl}_4/\text{Ne}$  mixtures, respectively. The symbols are the actual results and the lines are the linear fits to the "data points." Our analysis is not rigorous and the data points in these figures show some scatter analogous to experimental data. The variation of the energy exchange rate coefficient with  $\text{CCl}_4$  concentration is clear. The results indicated by triangles are for the choice  $p = 0.726$ , which is the value used by Warman and Sauer.<sup>25</sup> The results for the circles are the present choice,  $p = 1.38$ , which corresponds to the power law fit of the attachment cross section used here. The intercepts of the straight lines in Figs. 10(A) and 10(D) coincide reasonably well with the  $K_E$  values of pure Ar and pure Ne, respectively. The energy relaxation rate coefficient for electrons in a pure inert gas can be obtained from the Fokker-Planck operator and is given by

$$K_E = \frac{16\pi N_2 m}{3M_2} \sqrt{2KT_b/m} \int_0^\infty \exp(-x^2) x^5 \sigma_m(x) dx. \quad (19)$$

We find that  $K_E$  is  $0.87 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  and  $0.80 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  for Ar and Ne, respectively. Warman and Sauer<sup>25</sup> reported the values of  $0.13 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  and  $0.25 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  whereas Shimamori and Sinagawa<sup>26</sup> give the value of  $(10^{-13} - 10^{-14}) \text{ cm}^3 \text{ s}^{-1}$  for Ar. The experimental results are somewhat below the theoretical estimates. The intercepts in Fig. 10(B) give  $K_E$  values somewhat smaller than that given by Eq. (19), whereas the intercepts in Fig. 10(D) for Ne are in reasonable agreement with Eq. (19).

The slopes of the straight lines give  $K_E$  values for  $\text{CCl}_4$  and these depend on the assumed power law for the attachment cross section, Eq. (14). The slopes of the lines for both Ar and Ne give for pure  $\text{CCl}_4$  the  $K_E$  values of  $5 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  and  $3.8 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  for  $p = 0.726$  and  $1.38$ , respectively. Shimamori and Sinagawa recently reported the experimental estimate of  $10^{-7} \text{ cm}^3 \text{ s}^{-1}$  for  $K_E$  for pure  $\text{CCl}_4$ , which is about a factor of 2 larger than the estimates from Fig. 10. The exponential decay of the average energy given by Eq. (12) is not valid if the distribution function is not Maxwellian. Since the initial distribution is a delta function and the distribution is far from equilibrium, Eq. (13) used by Warman and Sauer is not a rigorous relationship between  $p\tau_{1,1}$  and  $K_E$ .

The electron distribution functions for  $\text{CCl}_4/\text{Ar}$  and  $X_{\text{CCl}_4} = 10^{-4}$  are shown for different times in Figs. 11(A)–11(C). Figure 11(D) is the steady distribution without attachment. The effect of the vibrationally inelastic collisions is clearly evident in these graphs especially at short times. The momentum transfer collisions serve at later times to broaden

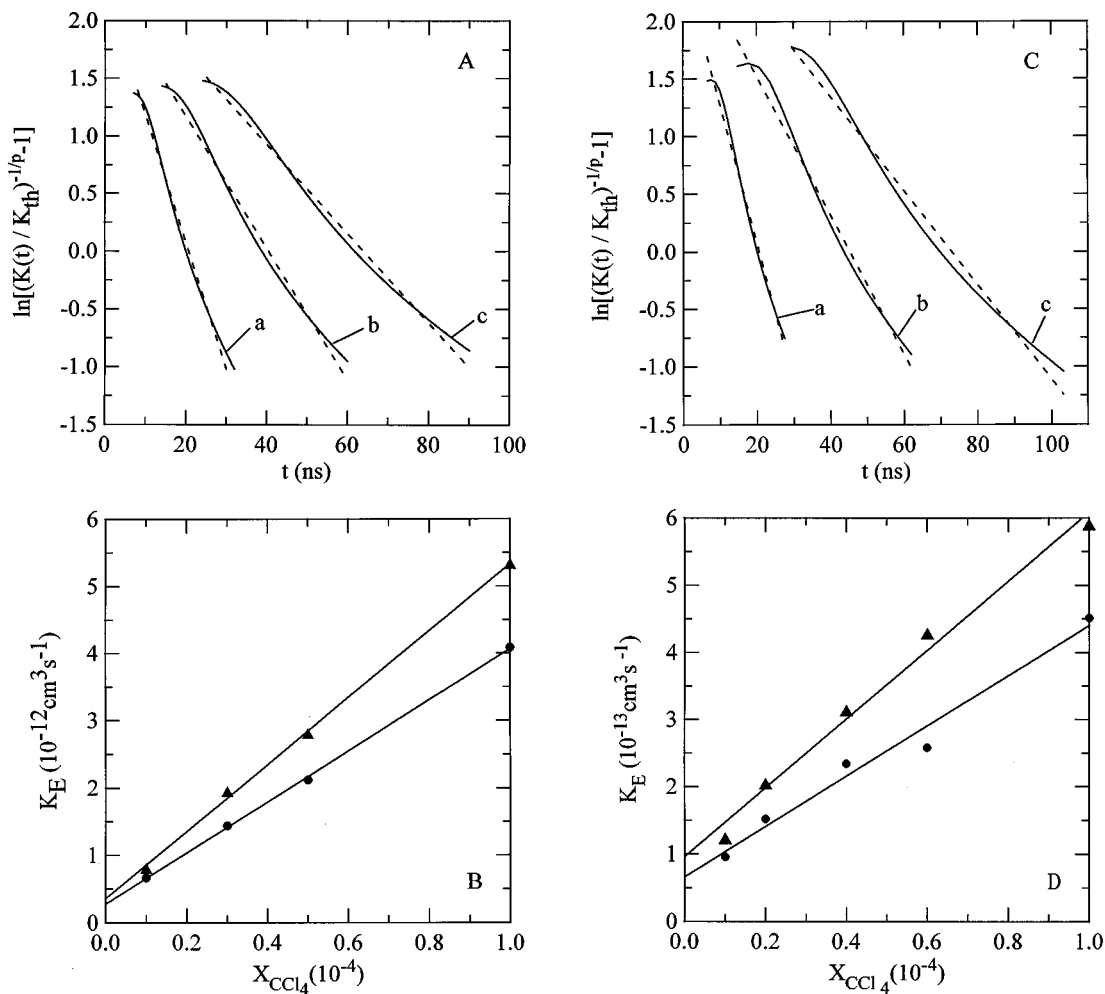


FIG. 10. The variation of the attachment rate coefficient versus time and the extraction of energy relaxation rate coefficients. (A) Variation of  $\ln[(k(t)/k_{th})^{-1/p} - 1]$  versus time for  $\text{CCl}_4/\text{Ar}$  mixtures. The dashed lines are linear fits to the calculations. The slopes yield approximate energy relaxation rate coefficients analogous to those determined experimentally. The mole fraction of  $\text{CCl}_4$  are (a)  $10^{-4}$ , (b)  $5 \times 10^{-5}$  and (c)  $3 \times 10^{-5}$ . (B) The concentration dependence of the energy relaxation rate coefficients from (A). The triangles are for  $p=0.726$  and the solid dots are for  $p=1.38$ . (C) Variation of  $\ln[(k(t)/k_{th})^{-1/p} - 1]$  versus time for  $\text{CCl}_4/\text{Ne}$  mixtures. The dashed lines are linear fits to the calculations. The slopes yield approximate energy relaxation rate coefficients analogous to those determined experimentally. The mole fraction of  $\text{CCl}_4$  are (a)  $10^{-4}$ , (b)  $4 \times 10^{-5}$  and (c)  $2 \times 10^{-5}$ . (D) The concentration dependence of the energy relaxation rate coefficients from (C). The triangles are for  $p=0.726$  and the solid dots are for  $p=1.38$ .

out the distribution function. At intermediate times ( $t=8$  ns), the distribution function is peaked at about 0.7 eV and shows some oscillations caused by the inelastic cross sections. The peak is bigger with attachment [Fig. 11(C)] than without attachment [Fig. 11(D)]. The effect of the attachment process is to remove low energy electrons and create a distribution function with a pronounced peak at high energies is also clearly seen in these graphs for the longer time of about 40 ns.

## V. THE STEADY ELECTRON DISTRIBUTION AT LONG TIMES

The main interest in this paper is the time scale for the approach of the electron distribution to a steady state as governed by elastic, the vibrationally inelastic and electron attachment collisions. The results are summarized in Tables I and II in terms of the  $\tau_{1,1}$  relaxation times. In this section, we

reconsider the calculations in the recent paper by Kowari and Shizgal<sup>24</sup> regarding the establishment of a steady electron distribution. The conclusions stated in this previous paper were based on calculations with an incorrect cross section. In Fig. 12, the  $e\text{-CCl}_4$  attachment cross section in the low energy region is shown. The curve labelled (b) is the cross section used in this paper as discussed in Section III. The curve labelled (a) is the cross section which results from a linear extrapolation of the actual cross section below 0.10 eV.

Figure 13 shows the time dependence of the average electron energy in an  $\text{CCl}_4/\text{Ar}$  mixture with  $X_{\text{CCl}_4} = 5 \times 10^{-6}$  for both attachment cross sections shown in Fig. 12. Cross-section (b) gives a steady distribution whereas cross-section (a) appears not to yield a steady state. We here elaborate on the interpretation of the different behavior obtained with these two attachment cross sections. In fact, both cross sec-

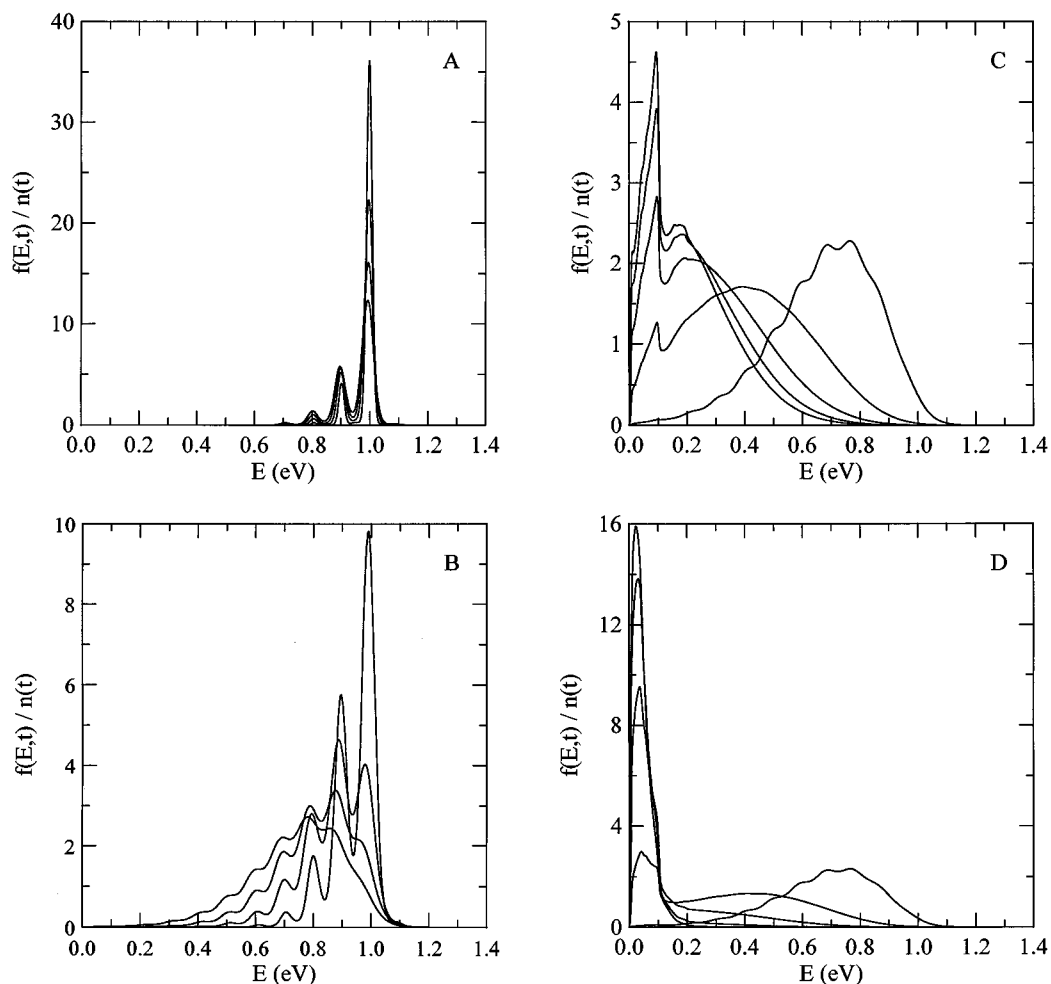


FIG. 11. Time dependence of the electron distribution function for electrons in a  $\text{CCl}_4/\text{Ar}$  mixture.  $X_{\text{CCl}_4} = 10^{-4}$ . (A) The time is from 0.32 ns to 1.28 ns in intervals of 0.32 ns. (B) The time is from 1.6 ns to 6.4 ns in intervals of 1.6 ns. (C) The time is from 8 ns to 40 ns in intervals of 8 ns. (D) Same as (C) but without attachment.

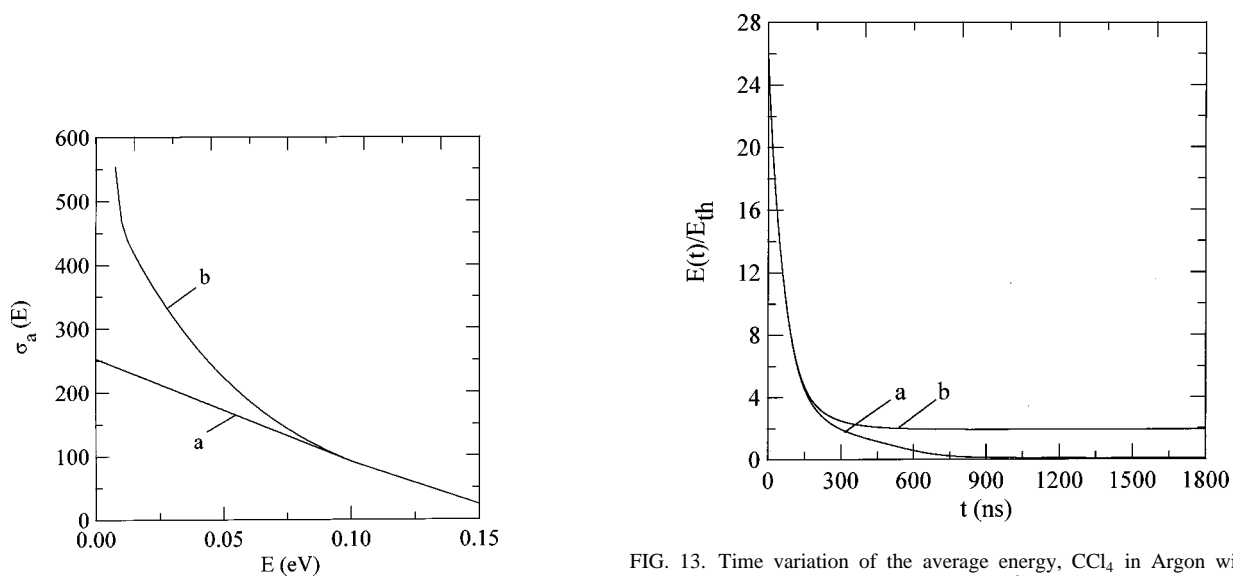


FIG. 12. Electron attachment cross section,  $e\text{-CCl}_4$ : (a) cross section used by Kowari and Shizgal, (b) cross section used in the present work.

FIG. 13. Time variation of the average energy,  $\text{CCl}_4$  in Argon with all collision processes included,  $X_{\text{CCl}_4} = 5 \times 10^{-6}$ . (a) Results for the attachment cross section used by Kowari and Shizgal, Fig. 12(a). (b) Results for the attachment cross section used in the present work, Fig. 12(b).

tions give a steady electron distribution; one, (b), leads to a high steady state temperature with  $T_{steady} > T_b$ , that is, attachment heating occurs, whereas the other cross section, (a), leads to a low steady state temperature with  $T_{steady} < T_b$ , that is electron cooling occurs.

Since the electron density decays to zero, there is no rigorous steady state. However, previous studies,<sup>21-23</sup> which neglected vibrationally inelastic collisions, demonstrated that a quasi-steady state can occur associated with the phenomenon of attachment heating. The phenomena of attachment heating as well as cooling have been discussed at length by Ness and Robson,<sup>38</sup> Robson<sup>39</sup> and by Shizgal.<sup>21-23</sup> This is very similar to the discussions of high and low temperature steady states in hot atom chemistry.<sup>40,41</sup> Although the attachment process removes electrons from the system, the electron distribution can attain a steady value with a steady average energy per electron. The analysis of these papers is based on the solution of the linear Fokker-Planck equation for the problem.

The electron velocity distribution function can be written as a sum of the eigenfunctions of the Fokker-Planck operator,<sup>21-23</sup>  $L$ , and is given by

$$f(x, t) = \sum_n f_n e^{-\lambda_n t} \psi_n(x), \quad (20)$$

where  $L\psi_n = \lambda_n \psi_n$ ,  $x = \sqrt{E/kT_b}$  is the reduced speed, and the  $f_n$  coefficients are determined from the initial distribution function. The electron number density and the energy are written in the form,

$$n(t) = \sum_{n=0}^{\infty} a_n e^{-\lambda_n t}, \quad (21)$$

$$\frac{E_{total}(t)}{E_{th}} = \sum_{n=0}^{\infty} b_n e^{-\lambda_n t}. \quad (22)$$

The average energy per electron is then

$$\begin{aligned} \frac{E(t)}{E_{th}} &= \frac{E_{total}(t)}{n(t)E_{th}} \\ &= \frac{b_0 e^{-\lambda_0 t} + b_1 e^{-\lambda_1 t} + \dots}{a_0 e^{-\lambda_0 t} + \dots}. \end{aligned} \quad (23)$$

With the assumption that the electron density decays to zero faster than the energy attains some steady state the long time dependence of the average energy per electron is

$$\frac{E(t)}{E_{th}} \approx \frac{b_0}{a_0} + \frac{b_1}{a_0} e^{-(\lambda_1 - \lambda_0)t} \quad (24)$$

provided that the higher order exponential terms  $(\lambda_0 - \lambda_n)$  are all much larger than the lowest one shown in Eq. (23).

In Fig. 14, we show the time dependence of the average electron energy and *without vibrationally inelastic collisions*. Curves (a) and (b) are for a  $\text{CCl}_4/\text{Ne}$  mixture for the attachment cross sections (a) and (b), respectively. Cross section (b) gives a steady state characterized by attachment heating whereas cross section (a) gives a low temperature steady state. Figure 14(A) illustrates for a relatively small  $\text{CCl}_4$  con-

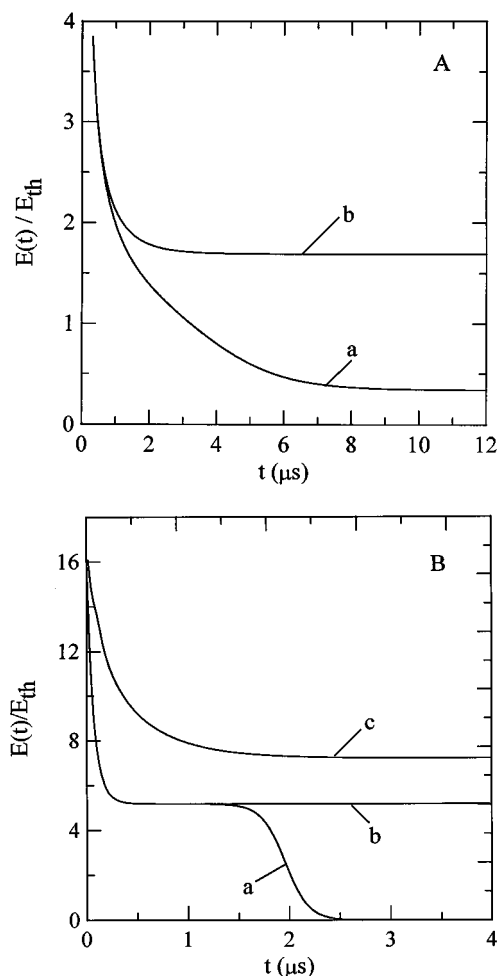


FIG. 14. Time variation of the average energy, without vibrationally inelastic collisions. (A)  $\text{CCl}_4$  in neon,  $X_{\text{CCl}_4} = 4 \times 10^{-7}$ . (a) Results for the attachment cross section used by Kowari and Shizgal, Fig. 12(a). (b) Results for the attachment cross section used in the present work, Fig. 12(b). (B)  $X_{\text{CCl}_4} = 2 \times 10^{-5}$ ; (a)  $\text{CCl}_4$  in Neon; results for the attachment cross section used by Kowari and Shizgal, Fig. 12(a). (b)  $\text{CCl}_4$  in neon; results for the attachment cross section used in the present work, Fig. 12(b). (c)  $\text{CCl}_4$  in argon with both cross sections in Fig. 12.

centration the attachment cooling effect. Curve (b) in the figure is for the cross section (b) and attachment heating occurs, with the asymptotic steady electron energy given by,  $E(\infty)/E_{th} = 1.69$ . Curve (a) is for cross section (a) and there is a low temperature steady state (attachment cooling) such that  $E(\infty)/E_{th} = 0.34$ . In Fig. 14(B) curve (c) is for a  $\text{CCl}_4/\text{Ar}$  mixture ( $X_{\text{CCl}_4} = 2 \times 10^{-5}$  and yields a high temperature steady state for *both* attachment cross sections. At first sight, one would be inclined to interpret the results as there being a steady electron distribution for  $\text{CCl}_4/\text{Ar}$  for both attachment cross sections and for  $\text{CCl}_4/\text{Ne}$  only for cross section (b). However, this interpretation is not correct as there are steady distributions for all three cases in Fig. 14. The steady values for the average energy,  $E(\infty)/E_{th}$  are 5.184 and 0.00359 for curves (b) and (a), respectively.

Figure 15 shows the change in the average electron energy for  $\text{CCl}_4/\text{Ne}$  mixtures versus the mole fraction  $\text{CCl}_4$  for

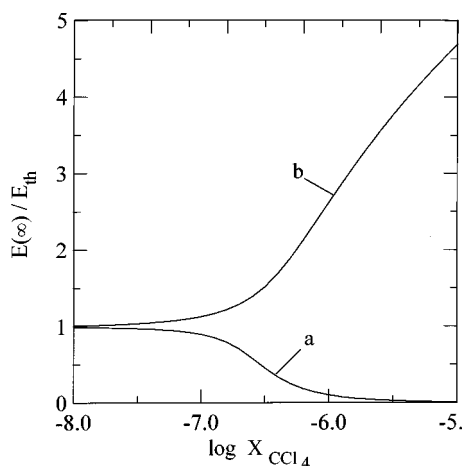


FIG. 15. The attachment heating and cooling effects for electrons in  $\text{CCl}_4/\text{Ne}$  mixtures without vibrationally inelastic collisions. (a) Results for the attachment cross section used by Kowari and Shizgal, Fig. 12(a). (b) Results for the attachment cross section used in the present work, Fig. 12(b).

both cross sections. For cross section (a) there is clearly a cooling of the electrons whereas for cross section (b) there is a heating. Cross section (b) leads to a hot steady state situation or attachment heating, whereas cross section (a) yields a cold steady state or electron cooling.

The steady distribution is given by the eigenfunction of the Fokker–Planck operator with the lowest eigenvalue. These eigenfunctions can be interpreted as eigenfunctions of a Schrödinger equation with a potential function determined from the Fokker–Planck operator. This potential which determines the nature of the spectrum of the operator depends on the energy dependence of the momentum transfer and attachment cross sections as well as the mass of the inert gas moderator. For  $\text{CCl}_4/\text{Ar}$ , there is only electron heating for both cross sections and we get the same results with either one. The low energy portion of the attachment cross section is not sampled. For  $\text{CCl}_4/\text{Ne}$ , it appears that the cross section (a) gives a low temperature steady state.

The time dependence of the average electron energy for cross section (a) shown in Fig. 14 depends on the eigenvalues and the density and energy coefficients,  $a_n$  and  $b_n$ , which are determined by the eigenfunctions. If there is a high temperature steady state (attachment heating) the lowest eigenfunction,  $\psi_0(x)$ , (the steady distribution) is displaced to higher energies with increasing  $\text{CCl}_4$  concentrations. This is shown in Fig. 16(B) for cross section (b). On the other hand, if there is a low temperature steady state (attachment cooling) the lowest eigenfunction (the steady distribution) is displaced towards lower energies with increasing  $\text{CCl}_4$  concentrations as shown in Fig. 16(A). The accompanying density and energy coefficients can be small. Several of the higher eigenfunctions can also be concentrated at lower energies. The time variation of the average energy for Fig 14(B), curve (a), can be interpreted as follows. With increasing  $\text{CCl}_4$ , the eigenvalue  $\lambda_0$  approaches  $\lambda_1$ , so that after an initial transient the average electron energy attains a nearly time independent value given by the ratio  $(b_0 + b_1)/a_0$  in Eq. (24). The exponential term over this time period from about  $0.4 \mu\text{s}$  to al-

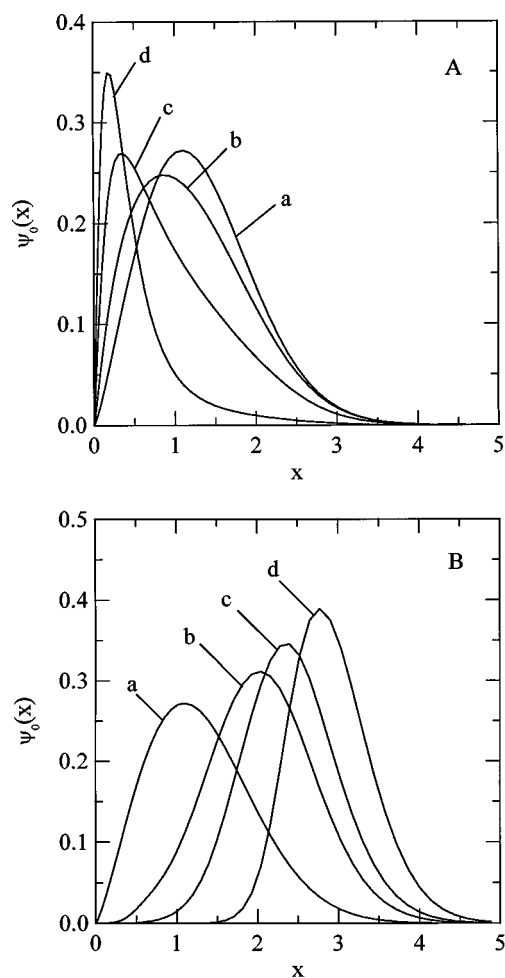


FIG. 16. Steady electron distribution functions as the lowest eigenfunction of the Fokker–Planck operator;  $\text{CCl}_4$  in neon without vibrationally inelastic collisions. (A) Results for the attachment cross section used by Kowari and Shizgal, Fig. 12(a).  $X_{\text{CCl}_4}$  equal to (a) 0, (b)  $10^{-7}$ , (c)  $2 \times 10^{-7}$  and (d)  $4 \times 10^{-7}$ . (B) Results for the attachment cross section used in the present work, Fig. 12(b).  $X_{\text{CCl}_4}$  equal to (a) 0, (b)  $5 \times 10^{-7}$ , (c)  $10^{-6}$  and (d)  $5 \times 10^{-6}$ .

most  $1.5 \mu\text{s}$  is essentially unity so that  $E(t)/E_{th} = 5.18$ , corresponding to the plateau value in Fig. 14. However, for times greater than about  $1.5 \mu\text{s}$  the exponential decays rapidly and  $E(t)/E_{th} = b_0/a_0 = 0.00359$ . In terms of the time dependent distribution function, one can say that it gets trapped briefly in an unstable high temperature state and then decays into the actual low temperature stable state at very long times.

The preceding discussion is based on the Fokker–Planck equation without vibrationally inelastic collision terms. The Boltzmann equation with inelastic collisions is also linear and a discussion in terms of the eigenvalues and eigenfunctions is possible analogous to the one just presented. The results shown in Fig. 13 for the systems with inelastic collisions could presumably be interpreted similarly. The absence of a plateau for curve (a) is presumably due to the influence of the inelastic terms in shortening the relaxation time and hence the difference in the two lowest eigenvalues is much larger in this case than for the model problem considered.

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