Boltzmann analysis of electron swarm parameters in CF₄ using independently assessed electron-collision cross sections

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(Received 1 March 1999; accepted for publication 2 July 1999)

Using independently assessed electron-collision cross sections, electron swarm parameters were calculated via the solution of the Boltzmann equation under the hydrodynamic regime. The cross sections used for the calculations were from a previously published assessment of electron-CF₄-collision cross sections that was recently updated. All of the cross sections used are based on published measurements (except those for direct vibrational excitation), and were not modified during the calculations to improve agreement between the calculated swarm parameters and the experimental values. Agreement between calculated and measured values of the swarm parameters was good for the drift velocity in pure CF_4 and in mixtures with argon, for the transverse diffusion coefficient in pure CF_4 , for the longitudinal diffusion coefficient in pure CF_4 and in mixtures with argon, and for the electron attachment coefficient in pure CF4. Agreement is poor for the ionization coefficient in CF_4 at most electric field-to-gas density ratios. The mostly reasonable agreement between the measured and calculated electron swarm parameters using the independently assessed cross sections validates the cross sections and the model. The use of independently assessed cross sections removes the potential arbitrariness and lack of uniqueness that often characterize cross section sets derived from Boltzmann analyses. Conjectures as to possible reasons for the lack of agreement between the calculated and measured values of the ionization coefficient are discussed. © 1999 American Institute of Physics. [S0021-8979(99)08519-9]

I. INTRODUCTION

Carbon tetrafluoride (CF₄) is a man-made gas with a wide variety of technological applications, including plasma etching of semiconductor materials, pulse power switching, gaseous dielectrics, and particle detectors. For plasma processing applications, CF₄ serves as a source of reactive species, such as ions and radicals, which are largely responsible for surface reactions in various etching and deposition processes. The CF₄ molecule is attractive for these applications because it is relatively inert in its electronic ground state, it has no stable excited electronic states, and the fragments formed upon dissociation are desirable active species in reactive ion etching processes.

The use of numerical modeling can be very useful in improving the understanding of the physics and chemistry inherent in the CF₄ discharges, and for helping to enhance the performance of these discharges in industrial applications.² However, an accurate knowledge of basic data, such as electron–molecule interaction cross sections and electron–transport parameters is necessary to perform useful calculations. Fortunately, a significant amount of electron–molecule interaction data is available in the literature for CF₄.

Several efforts^{1,3,4} to provide sets of electron-CF₄ interaction data based upon experimental measurements have been published in recent years, primarily in an effort to address the modeling needs of the semiconductor community. The most recent of these reviews by Christophorou et al.¹ (recently updated⁵ to incorporate the results of several measurements since its publication in 1996) provides a comprehensive assessment and evaluation of all electron-interaction data for CF₄. The recommended cross sections from this review provide a reasonably complete "set" of electroninteraction data for CF₄ for electron energies ranging from 0.003 to 1000 eV. These data were derived directly from an assessment of experimental measurements. Also contained in the review^{1,5} are recommended values of electron transport (swarm) parameters, such as drift velocities, ionization and attachment coefficients, and electron diffusion coefficients. These were similarly based upon an assessment of the available experimental data.

The recommended cross sections determined by Christophorou *et al.*^{1,5} are self-consistent in the sense that when the recommended cross sections of the various processes are summed together they reproduce the independently measured total scattering cross section, within experimental uncertainties. However, within the scope of that review¹ the authors did not conduct an additional consistency check of the data, namely using the recommended cross sections and the Boltzmann equation to calculate electron swarm param-

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eters for comparison with the values recommended from the assessed experimental data. This is done in this paper. A similar, but limited, effort was recently published by Vasenkov⁶ using a Monte Carlo calculation.

The cross section set used here for the calculations is based upon the previously published assessment of electron- CF_4 -collision cross sections¹ and the recently published update⁵ of the indirect vibrational excitation cross section, the total ionization cross section, and the cross section for dissociation into neutrals. All of the cross sections used were determined from the assessment of published measurements, and were not modified during the calculations. In other words, no iterative process was used to modify the cross sections to improve agreement between the calculated swarm parameters and the recommended values. This differs from similar calculations performed previously, as will be discussed later in this paper. Comparisons are presented between the Boltzmann-calculated values and the measured values of various electron swarm parameters for a range of electric field-to-gas density ratios, (E/N) from 0.03×10^{-17} to 600×10^{-17} V cm² (0.03–600 Td). Analysis of the areas of agreement and disagreement between the calculated and recommended swarm parameter data^{1,5} allows a reasonable discussion concerning the validity of the cross sections and the appropriateness of the Boltzmann code used.

A number of cross section data sets for electron interactions with CF₄ have been derived by Boltzmann modeling of electron swarm parameters.^{7–11} In contrast to the present work, these investigations assumed an initial electroninteraction cross section set, and then modified the set iteratively until the electron transport parameters calculated by solving the Boltzmann equation agreed with independent measurements of the swarm parameters. A difficulty of this procedure is that the derived electron-interaction cross section set is not a unique solution (the solution being constrained only by the required agreement with experimental swarm parameters). If little is known concerning the cross sections for a given molecule, then cross sections and/or processes that are not physically meaningful may be included in the derived set.

The recent work of Bordage *et al.*⁷ included the most extensive study of existing data on electron interactions with CF_4 to be used in a Boltzmann calculation, and made the most concerted effort to use these data as an initial constraint in a physically consistent manner. This calculation, which included effects due to superelastic collisions and the anisotropy of the electron energy distribution, produced good agreement with independently measured electron swarm data. However, the final cross section set derived by this calculation⁷ differs significantly from the cross section set recommended by the review of Christophorou *et al.*^{1,5} This discrepancy highlighted the need to perform similar Boltzmann calculations using the recommended cross section data from Refs. 1 and 5.

The primary purpose of the work presented here is to use Boltzmann modeling to show the consistency of the recommended cross sections and electron swarm parameters of Christophorou *et al.*^{1,5} Additionally, we use the results of this investigation to: (1) evaluate the validity of the calculation for the determination of swarm parameters in CF₄; (2) evaluate potential deficiencies of the cross sections, and (3) address the discrepancies between the cross sections deduced by Christophorou *et al.*¹ and those derived by Bordage *et al.*⁷ The observed agreement between the measured and calculated swarm parameters clearly validates the cross section set used, and demonstrates the importance of basing cross section sets on independent measurements.

II. CROSS SECTIONS AND SWARM PARAMETERS

The electron-interaction cross sections for CF_4 recommended in the review by Christophorou *et al.*¹ were derived from a thorough analysis of the data available in the literature in 1996. These include cross sections for total electron scattering, elastic momentum transfer, integral elastic scattering, direct vibrational excitation, indirect (resonance enhanced) vibrational excitation, electron attachment, ionization, and dissociation into neutrals. Some of these values were recently updated by Christophorou and Olthoff.⁵ The basis of the cross sections recommended by Christophorou *et al.*^{1,5} is briefly summarized here, but the reader is referred to Refs. 1 and 5 for a detailed discussion of the original assessment.

Above 1 eV, the recommended total scattering cross section $\sigma_{sc,t}(\varepsilon)$ was derived from three independent measurements,^{12–14} all of which are in agreement. Below 1 eV, the recommended total scattering cross section was deduced by adding the elastic scattering cross section of Mann and Linder¹⁵ and the direct vibrational excitation cross sections of Bonham.³ This derivation agrees well with the few experimental data points of Szmytkowski *et al.*¹³ available at energies below 1 eV, and the recent direct experimental measurements of $\sigma_{sc,t}(\varepsilon)$ by Lunt *et al.*¹⁶ at 0.003 eV.

The recommended elastic momentum transfer cross section $\sigma_m(\varepsilon)$ and the recommended integral elastic cross section $\sigma_{e,int}(\varepsilon)$ were derived from three experimental measurements: those of Mann and Linder¹⁵ below 0.5 eV, and those of Sakae *et al.*¹⁷ and Boesten *et al.*¹⁸ for electron energies above 1.5 eV. An interpolation was used in the energy range between 0.5 and 1.5 eV, where no data were available.

The recommended cross sections for direct vibrational excitation $\sigma_{\rm vib,dir}(\varepsilon)$ of the ν_3 and ν_4 modes (the only infrared active modes) were derived from the Born-dipole approximation performed by Bonham,³ as a complete direct measurement is not available. However, a direct measurement¹⁹ of $\sigma_{\rm vib,dir}(\varepsilon)$ at 2 and 3 eV agrees well with the cross section calculated from the Born-dipole approximation.

The recommended cross section for total ionization $\sigma_{i,l}(\varepsilon)$ is derived from the new measurements of Rao and Srivastava²⁰ and Nishimura *et al.*²¹ along with two previously available measurements of $\sigma_{i,t}(\varepsilon)$.^{22,23} The recommended values of $\sigma_{\text{diss,neut},t}(\varepsilon)$ are based upon the new absolute measurements of Mi and Bonham²⁴ and the new relative measurements of Motlagh and Moore.²⁵

The cross section recommended in Ref. 5 for indirect (resonance enhanced) vibrational excitation $\sigma_{\text{vib,indir},t}(\varepsilon)$ is deduced by subtracting the recommended cross sections for



FIG. 1. (a) The independently assessed cross section set for electron interactions with CF_4 from Refs. 1 and 5. (b) The cross section set used by the multiterm Boltzmann code discussed in Sec. III. The solid points are the recommended data from curves (a). The lines represent the fits used in the Boltzmann calculation described in Sec. III.

direct vibrational excitation, elastic scattering, and dissociative attachment from the total scattering cross section. While this technique is valid, it has the potential for significant uncertainties. Additional measurements of $\sigma_{\rm vib,indir,t}(\varepsilon)$ to reduce the uncertainty of this cross section are needed due to its large influence on the calculated swarm parameters (discussed further in Secs. IV and V). These measurements could either take the form of new measurements of $\sigma_{e,int}(\varepsilon)$ to reduce the uncertainty of the deduced value of $\sigma_{\rm vib,indir,t}(\varepsilon)$, or direct measurements of $\sigma_{\rm vib,indir,t}(\varepsilon)$.

Figure 1(a) shows the recommended cross section set derived by Christophorou *et al.*^{1,5} for electron interactions with CF_4 . The data in this figure are the basis for the cross sections used in the Boltzmann code discussed in Sec. III to calculate the swarm parameters.

The lines in Fig. 1(b) show a graphical representation of the cross section data as used in the Boltzmann calculations discussed in Sec. III. These data are spline fits to the recommended data discussed earlier, but have been extended to thresholds or larger energy ranges where appropriate. The solid symbols are the values given in the recommended data set shown in Fig. 1(a). Values for $\sigma_{i,t}(\varepsilon)$, $\sigma_{\text{diss,neut},t}(\varepsilon)$, and $\sigma_{\text{vib,indir},t}(\varepsilon)$ are taken from Table 1 of Ref. 5, and values for $\sigma_m(\varepsilon)$, $\sigma_{\text{vib,dir},t}(\varepsilon)$, and $\sigma_{a,t}(\varepsilon)$ are taken as presented in Tables 5, 9, and 25, respectively, of Ref. 1. The cross sections for $\sigma_{\text{sc},t}(\varepsilon)$ and $\sigma_{e,\text{int}}(\varepsilon)$ are not used directly in the calculation. The cross sections for vibrational excitation are cut off at 100 eV because values above this energy do not affect the calculations for the range of E/N values studied here.

At this point it is useful to briefly consider the use of the word "set" when referring to a collection of electroninteraction cross sections for a specific gas. Ordinarily the use of the word set implies that the cross sections reflect a complete representation of all possible (or significant) electron-interaction processes. In this sense, the recommended cross sections of Christophorou and co-workers^{1,5} for CF₄ may be considered as a set since sufficient experimental data are available for the most significant processes. For the remainder of this paper, we will use the term set when referring to the updated, independently assessed cross sections of Christophorou et al. derived in Refs. 1 and 5, since they will be used as such in the calculation described in Sec. III. Additionally, we will use the word set when discussing collections of cross sections derived from Boltzmann analyses. It is important to realize that the cross sections derived as a set from Boltzmann analyses, while independent of the chosen numerical method, depend upon the approximations made. Thus the individual cross sections of a Boltzmann-derived set may be considered only with the other cross sections of the set, and often only in the same model (or calculation) from which they were derived. Such is not the case for cross section sets based upon assessments of independently measured cross sections.

The swarm parameters calculated later in this paper are the electron drift velocity w(E/N) in CF₄ and in mixtures of CF₄ and Ar; the transverse electron diffusion coefficient to electron mobility ratio $D_T/\mu(E/N)$ in CF₄; the product of the number density and the longitudinal electron diffusion coefficient $ND_L(E/N)$, in CF₄ and in mixtures of CF₄ with Ar; the density-reduced electron attachment coefficient $\eta/N(E/N)$ in CF₄; and the density-reduced electron-impact ionization coefficient $\alpha/N(E/N)$ in CF₄. These calculations are compared to the recommended electron swarm data from Refs. 1 and 5, except for $ND_L(E/N)$, for which the comparison is made to the recent measurements of Hayashi and Nakamura.¹¹

III. CALCULATION

A detailed discussion of the Boltzmann-based calculation used in this work to derive values of the swarm parameters may be found elsewhere,^{7,26} but a brief description is provided here. The calculation of swarm parameters is based on the numerical solution of the Boltzmann equation under the approximation of the hydrodynamic regime as developed some years ago in a systematic way by Kumar, Skullerud and Robson.²⁷ In this approximation, the initial Boltzmann equation, which depends on time, space, and velocity variables, is transformed into an infinite set of equations which is only a function of the velocity variable. To obtain the swarm parameters of interest in this work only the first four equations have to be solved. Furthermore, to determine the ionization coefficient, a unique equation (derived from the whole set of hydrodynamic equations) is employed.⁷

These equations are solved with the help of a numerical method similar to the method developed in the field of neutron transport theory, whose main idea is to introduce a discrete approximation of the Boltzmann equation so that the main physical conservation properties are conserved.²⁸ As this numerical method is iterative (and in most cases requires a large number of iterations), a specific acceleration procedure is introduced. This acceleration technique is based on the physical observation that the leading equation in the expansion of the distribution function into a series of Legendre polynomials corresponds to the well known two-term approximation and that the exact solution can be obtained by solving the two-term approximation equation corrected with an extra term, which is a function of the second anisotropy of the distribution function. This extra term is obtained from the finite element solution. It has been shown²⁹ that this acceleration procedure is very efficient and that, in most cases, the number of iterations become less that ten.

An interesting point of this technique is that there is no ab initio approximation in the solution of the Boltzmann equation. For example, the exact dependence of the electron distribution versus the velocity vector is fully taken into account. The accuracy of these calculations is then not limited by the accuracy of the numerical solution of the Boltzmann equation. Usually, in solving the hydrodynamic equations, it is assumed that all collisional processes are isotropic. However, as this assumption is never valid for elastic collisions, in our case, the elastic momentum transfer cross section is used instead of the integrated elastic cross section. It has been shown that because this choice for the elastic cross section is consistent with the momentum and energy equations, it gives accurate results and avoids the need to introduce the real elastic angular differential cross section. However, complete angular differential cross sections for all collisional processes can be introduced in the numerical calculation, if they are known.

A simple approximation is used for the energy distribution of electrons coming from ionization. In this approximation, it is assumed that the residual energy after ionization is shared by the two electrons according to a fixed ratio. Changing this ratio did not affect the results of our calculations in our working E/N range.

In our calculations, due to the low energy threshold of vibrational collisions, it is necessary to introduce superelastic collisions for these processes in order to avoid unphysical results. The number density of molecules in a vibrationally excited state is assumed to be determined by a Boltzmann distribution at room temperature. Another important point to be included is related to the calculation of the ionization coefficient at low E/N values and the correct determination of the maximum value of the energy of the electron distribution function. For a given value of E/N, the calculation of the ionization coefficient uses the high energy tail of the electron energy distribution function (EEDF) together with the first rising part of the ionization cross section. It follows that large changes in the ionization coefficient may be introduced by small errors in the tail of the EEDF, by errors in the onset of the ionization cross section, or by uncertainties in the shape of the ionization cross section near threshold. This TABLE I. Parameters for the Boltzmann code for each cross section.

Cross section	Threshold (eV)	Energy loss (eV)
Elastic Momentum, $\sigma_m(\varepsilon)$	0.0001	0.0
Direct Vibrational Excitation (ν_4), $\sigma_{vib,\nu4}(\varepsilon)$	0.078	0.078
Direct Vibrational Excitation (ν_3), $\sigma_{\text{vib},\nu_3}(\varepsilon)$	0.159	0.159
Indirect Vibrational Excitation, $\sigma_{\text{vib.indir.t}}(\varepsilon)$	4.0	0.4
Ionization, $\sigma_{i,t}(\varepsilon)$	15.9	15.9
Attachment, $\sigma_{a,t}(\varepsilon)$	4.3	4.3
Dissociation into Neutrals, $\sigma_{diss,neut,t}(\varepsilon)$	10.0	10.0

may account for the discrepancies discussed later in the paper.

A threshold energy and an energy loss is assigned to each collision cross section considered in the calculation. These are listed in Table I for the calculations performed here. The thresholds used here were determined from experimental measurements described in Ref. 1, except for $\sigma_m(\varepsilon)$, which is chosen at a very low energy (0.0001 eV) below thermal energies, and $\sigma_{\text{vib.indir,t}}(\varepsilon)$, which is set at 4.0 eV. The energy losses are routinely set to the threshold energies as a good approximation. The two exceptions to this are $\sigma_m(\varepsilon)$ which is assigned an energy loss of zero [actually, the elastic energy loss $\sim (2m/M)\varepsilon - kT_g$ is very small, even for electron energies of 100 eV, and may be ignored] and $\sigma_{\text{vib.indir,t}}(\varepsilon)$ whose energy loss is set at 0.4 eV based upon an assessment of the contributions from higher vibrational modes that are excited via the resonance.¹⁸

IV. RESULTS

In this section we present the values of several swarm parameters as calculated using the previously described Boltzmann-code model and the set of electron-collision cross sections^{1,5} discussed in Sec. II. and as shown in Fig. 1(b). These results are compared to the recommended values of the swarm parameters.^{1,5}

Figure 2(a) shows the variation of the calculated electron drift velocity w(E/N) for CF₄, as compared to the recommended values from Ref. 1 that were derived from the available experimental data. The agreement is excellent over much of the range of E/N, with discrepancies approaching 10% in the region between 10×10^{-17} and 100×10^{-17} V cm². Figure 2(b) shows similar data in various mixtures of CF₄ with argon. Agreement is better here than for the pure gas, except for values of E/N exceeding 100×10^{-17} V cm².

Figure 3(a) shows a comparison between the calculated values of the transverse electron diffusion coefficient and the recommended experimental values¹ for CF₄. The agreement is reasonably good over the entire range of E/N, with the largest discrepancies occurring near 10×10^{-17} V cm². Figure 3(b) shows the calculated values of the product of the longitudinal diffusion coefficient and the number density $ND_L(E/N)$ for CF₄ and for two mixtures with argon. These are compared with the recent experimental data of Hayashi and Nakamura.¹¹ Reasonable agreement is obtained between the calculated and experimental values for each gas mixture.



FIG. 2. (a) Comparison of calculated drift velocity (—) as a function of E/N for pure CF₄ with measured values (\bullet) from Ref. 1. (b) Comparison of calculated drift velocity (lines) as a function of E/N for mixtures of CF₄ and argon with measured values (symbols) from Ref. 30.

However, discrepancies in magnitude of up to 30% are evident for the pure CF₄ data between 10×10^{-17} and 100×10^{-17} V cm², the same range of *E/N* for which the most significant discrepancies were observed for w(E/N).

Figure 4 shows the values of the density-reduced electron attachment and ionization coefficients η/N and α/N as a function of E/N. The agreement between the calculated values of $\eta/N(E/N)$ and the recommended experimental values¹ is satisfactory for $E/N > 50 \times 10^{-17}$ V cm², but the calculated values are as much as an order of magnitude smaller than the calculated values at the lowest E/N. The calculated values of $\alpha/N(E/N)$ are in poor agreement with the recommended experimental values,⁵ agreeing only for values of E/N near 100×10^{-17} V cm² where the two curves cross. Potential causes of these significant disagreements are discussed in Sec. V.

V. DISCUSSION

In order to put the degree of agreement between our calculated swarm parameters and the recommended experimental values in perspective, it is useful to compare our present results with the previous results derived from the earlier Boltzmann analysis of Bordage *et al.*⁷ This includes, first, a comparison of the electron-collision cross sections



FIG. 3. (a) Comparison of calculated transverse electron diffusion coefficient to electron mobility ratio (—) as a function of E/N for pure CF₄ with recommended measured values (\bullet) from Ref. 1. (b) Comparison of calculated values of the product of the longitudinal electron diffusion coefficient and the gas number density (lines) as a function of E/N with measured values (symbols) from Ref. 11 for CF₄ and in two mixtures with argon.

used here^{1,5} and the cross section set derived by Bordage *et al.*,⁷ and second, a comparison of the swarm parameters calculated by using each cross section set in the same Bolt-zmann code.



FIG. 4. Comparison of the calculated density-reduced electron-impact ionization coefficient (—) as a function of E/N for pure CF₄ with the recommended measured values (\bullet) from Ref. 5, and comparison of the calculated density-reduced electron attachment coefficient (––) with recommended measured values (\blacksquare) from Ref. 1.



FIG. 5. Comparison of the independently assessed (IA) cross section set used in the present calculations (—) with the Boltzmann-derived (BD) cross section set used for similar calculations in Ref. 7 (––).

Figure 5 shows a comparison of the cross sections^{1,5} used in this work (solid lines) and those derived previously by Bordage *et al.*⁷ (dashed lines). For clarity in the remainder of the paper, the cross section set derived in Ref. 1 and updated in Ref. 5 will subsequently be referred to as the independently assessed (IA) cross section set. The cross section set derived previously by Bordage *et al.*⁷ by optimizing the agreement between the calculated and measured values of various swarm parameters will be referred to as the Boltzmann-derived (BD) cross section set. Significant differences are evident between the two sets for the cross sections

for elastic momentum transfer $\sigma_m(\varepsilon)$ and vibrational excitation $\sigma_{vib}(\varepsilon)$.

The difference between the cross sections for elastic momentum transfer [Fig. 5(a)] is significant below 10 eV, approaching factors of 100 for electron energies between 0.2 and 1 eV. The effects of this large difference in $\sigma_m(\varepsilon)$ on the calculated swarm parameters are significant and will be discussed later in this section. Clearly, the BD values⁷ of $\sigma_m(\varepsilon)$ are not in agreement with the measurements of Mann and Linder,¹⁵ upon which the IA values of $\sigma_m(\varepsilon)$ are based.

The differences in the vibrational excitation cross sections [Fig. 5(b)] are also substantial. At low energies, both cross section sets exhibit the same thresholds for direct vibrational excitation, but the BD set has a bump near 0.1 eV in the ν_4 excitation cross section that may compensate for some of the differences in the elastic momentum transfer cross sections. The most significant difference between the two cross section sets is the existence of the indirect vibrational cross section in the IA cross section set. While the lack of this cross section is somewhat accounted for in the BD cross section set by the broad peaks near 8 eV in the ν_3 and ν_4 excitation cross sections, there are several important differences between these two methods of treating vibrational excitation via the resonance at 8 eV.

First, the width of the peaks in the ν_3 and ν_4 excitation cross sections for the BD set are significantly larger than the width of the resonance. This is difficult to justify physically.

Second, the BD cross section set makes no distinction between indirect vibrational excitation processes and the direct vibrational excitation processes. This has the result of designating the same energy loss to direct and indirect vibrational excitation collisions. In reality, the longer interaction time of collisions occurring via the resonance enables significant excitation of higher harmonic modes,¹⁸ which results in larger average energy losses for the indirect excitation collisions. This larger energy loss greatly increases the impact of the indirect vibrational excitation cross section on the electron energy distribution function and hence on the calculated swarm parameters, which underscores the need for accurate cross section (both shape and magnitude) and energy loss measurements for this process.

Third, the angular distributions of scattered electrons are different for direct and indirect excitation processes. For indirect vibrational excitation, the angular distribution for scattered electrons is nearly isotropic, but for direct excitation it is strongly weighted toward forward scattering.¹⁸ While most Boltzmann calculations (including the ones presented here) do not take into account the angular distribution of electrons scattered from inelastic collisions, this may be an important consideration when considering the accuracies of the calculated swarm parameters. It is possible to include this effect in our calculations, but it requires a complete description of the differential scattering cross sections over all angles and all energies, which is presently not available.

The cross sections assumed by both cross section sets for the processes of dissociative attachment, ionization, and dissociation into neutrals [see Figs. 5(c), 5(d), and 5(e), respectively], are similar. In each case the differences are on the order of the uncertainties in the experimental measurements.



FIG. 6. Comparison of selected swarm parameters between the recommended measured values from Refs. 1 and 5 (\bullet), the calculated values using the IA cross section set (—), and the calculated values using the BD cross section set of Ref. 7 (––).

Figure 6 shows comparisons of the calculated values of the four main swarm parameters in CF_4 using both cross section sets. The solid lines are the calculations based upon the IA cross section set derived here, and are the same results presented in Figs. 2–4. The dashed lines are the results from the calculations published previously by Bordage *et al.*⁷ using the BD cross section. The solid circles are the recommended experimental data.^{1,5}

In general, the Boltzmann code does a reasonable job of calculating w(E/N) and $D_T/\mu(E/N)$ using either cross section set [see Figs. 6(a) and 6(b)], with the BD set providing slightly better agreement with the experimental data. The differences in the calculated values of w(E/N) and $D_T/\mu(E/N)$ in the E/N range of $10 \times 10^{-17} - 100 \times 10^{-17}$ V cm² are attributable to the differences in the values of $\sigma_m(\varepsilon)$ used.

The BD cross sections clearly produce a more accurate calculation of the density-reduced ionization coefficient



FIG. 7. Variation of the density-reduced ionization coefficient with different modifications to the IA cross section set. The modifications are described in the legend.

 $\alpha/N(E/N)$ than the IA cross sections. Analysis of the different momentum transfer cross sections used in each calculation indicates that the differences in $\sigma_m(\varepsilon)$ affect the magnitude of the calculated values of $\alpha/N(E/N)$ without affecting overall agreement. Therefore, the differences in the calculated values of $\alpha/N(E/N)$ can be attributed primarily to differences in vibrational excitation cross sections. For the density-reduced electron attachment coefficient $\eta/N(E/N)$ the levels of agreement between the experimental data and the calculated values are quite similar for both cross section sets, with the calculations from both sets exhibiting rather poor agreement with the experimental data at low E/N.

In general it can be stated that use of the IA cross section set enables the calculation of swarm parameters that are in reasonable agreement with experimentally derived values, with the exception of the ionization coefficient. However, even this level of agreement demonstrates the validity of the independently assessed cross sections. The fact that the BD cross section set produces values of swarm parameters that agree somewhat better with experimental results is expected since the BD cross section set was optimized to minimize the differences between the calculated and measured swarm parameters. The question of why the independently derived cross sections do not produce better agreement between the calculated and measured swarm parameters is an interesting one, particularly for $\alpha/N(E/N)$.

While the IA cross section set presented here was not modified to optimize the agreement between calculated and measured swarm parameters, an analysis of the effects of changing the cross sections and some of the other calculation parameters (e.g., threshold and energy loss values) within their uncertainties is useful and was performed. From this analysis it is obvious that the magnitude of $\sigma_{vib,indir,t}(\varepsilon)$, and the corresponding energy loss, exert significant influence on the calculated values of $\alpha/N(E/N)$. This is due to the effect of the cross section for indirect vibrational excitation $\sigma_{vib,indir,t}(\varepsilon)$ and the relatively large energy loss parameter associated with it, on the electron energy distribution function (EEDF), and thus indirectly on the calculated value of $\alpha/N(E/N)$ which depends on the product of the EEDF and $\sigma_{i,t}(\varepsilon)$.

The influence of $\sigma_{\text{vib,indir},t}(\varepsilon)$ is evident from Fig. 7, which shows how calculations of the density-reduced ionization coefficient are affected by changes in $\sigma_{\text{vib,indir},t}(\varepsilon)$ and the corresponding energy-loss parameter, but are unaffected by changes to other cross sections. The details of the modifications to the cross sections and collision parameters are shown in the legend of Fig. 7. The solid line shows the values of α/N as a function of E/N that were calculated from the cross sections and model parameters presented in Secs. II and III, and in Table I. These are the same values of $\alpha/N(E/N)$ shown in Fig. 4. The next two curves in Fig. 7 show the negligible effect of increasing or decreasing the total ionization cross section by 10%. Both of these curves are nearly superimposed on the solid curve. By contrast, increasing $(-\cdot -)$ or decreasing (---) the cross section for indirect vibrational excitation has a substantial effect on the magnitude of the calculated values of $\alpha/N(E/N)$. Similarly, decreasing the energy loss (-----) associated with indirect vibrational excitation collisions from 0.4 to 0.3 eV results in an even larger change in the calculated values of $\alpha/N(E/N)$. A reasonable modification to the width of the cross section for indirect vibrational excitation consistent with the physical characterization of the resonance, such as changing the threshold for the cross section from 4 to 3 eV, results in a change that is too small to differentiate from the initial calculations. All of the curves converge at E/N values above $200 \times 10^{-17} \,\mathrm{V \, cm^2}$.

The changes in the calculated values of $\alpha/N(E/N)$ shown in Fig. 7, due to the modifications to the cross sections listed in the legend, affect principally only the magnitude of the $\alpha/N(E/N)$ curve with little overall improvement in the comparison with the experimental values. Thus one can conclude that it is difficult to obtain good agreement between the calculated and measured values of $\alpha/N(E/N)$ by modifying the $\sigma_{\text{vib,indir},t}(\varepsilon)$ in this manner. Additional investigation of this apparent discrepancy is required.

Interestingly, changes in magnitude of the ionization cross section have little effect on the calculated ionization coefficients, at least when compared to the observed discrepancies between the measurements and the calculations, and when compared to the changes observed due to similar modifications to $\sigma_{\text{vib,indir,t}}$. This is consistent with the fact that $\alpha/N(E/N)$ depends primarily on the high energy tail of the EEDF, which is strongly influenced by the indirect vibrational excitation process. Thus, it becomes apparent that an accurate determination of $\sigma_{\text{vib,indir},t}(\varepsilon)$ is more important to the calculation of $\alpha/N(E/N)$ than an accurate determination of $\sigma_{i,t}(\varepsilon)$. As mentioned previously, the deduced value of $\sigma_{\text{vib,indir},t}(\varepsilon)$ possesses the largest potential uncertainty of all the cross sections in the independently derived set. This is due to the lack of experimentally derived vibrational excitation cross sections, the current method used to deduce this cross section, and the rather large uncertainties in the elastic scattering cross section in this general energy range. It may be that a more accurate determination of the shape of $\sigma_{\text{vib,indir},t}(\varepsilon)$ would result in better agreement between the calculated and measured values of $\alpha/N(E/N)$.

There are many other potential causes for the discrepancies between the calculated and measured swarm parameters that require further investigation. First, there is potential for errors in the experimentally derived data other than $\sigma_{\text{vib,indir},t}(\varepsilon)$. For example, the experimentally derived values of $\sigma_m(\varepsilon)$ and $\sigma_{e,int}(\varepsilon)$ are determined by the integration over all scattering angles, which necessitates an extrapolation to large scattering angles beyond those measured. Accurate measurements of large-angle scattering would help reduce the uncertainties of these cross sections. Interestingly, with the exception of $\alpha/N(E/N)$, all of the swarm parameters calculated here agree best with the measured values when using the $\sigma_m(\varepsilon)$ values of the BD set with the values of the other cross sections from the IA set.^{1,5} This could be interpreted to mean that the measured values of $\sigma_m(\varepsilon)$ are in significant error at low energies. However, the differences between the BD momentum transfer cross section and the measured values of $\sigma_m(\varepsilon)$ are too great to be attributed to experimental error, suggesting that other sources of error exist that can be incorrectly compensated for by changing $\sigma_m(\varepsilon).$

Another potential source of error is that the cross section for dissociation into neutrals remains unverified, and the uncertainties in the present measurements could be substantial, particularly at electron energies near threshold. Furthermore, while the experimental values of the swarm parameters are generally considered to be well known, the uncertainties in these measurements could account for some of the discrepancies between calculations and experiments, especially at low E/N.

Another potentially important point to consider is that all of the experimental data used in this paper, both cross sections and swarm parameters, were obtained under conditions where vibrationally excited species could exist in substantial quantities. The effects of these vibrationally excited species are in many cases unknown, and the Boltzmann codes do not take these species into account except for the case of superelastic collisions between electrons and excited CF_4 molecules.⁷

Finally, the angular distribution of electrons scattered in inelastic collisions is not taken into account by the Boltzmann calculation used here (as indicated earlier in this paper, the distribution from elastic collisions is accounted for by using the momentum transfer cross section rather than the integral elastic cross section). The angular distribution of electrons scattered from direct vibrational excitation collisions is heavily weighted toward forward scattering, and the effect of this behavior on the calculation of the electron energy distribution in the swarm could be considerable. Complete differential cross sections for inelastic processes are necessary to implement this aspect of the calculation.

VI. CONCLUSIONS

An independently assessed set of cross sections^{1,5} for electron interactions with CF_4 , derived from the most reliable measurements presently available, has been used in a multi-term Boltzmann code in order to calculate various swarm parameters for electrons in pure CF_4 and in its mix-

tures with argon. This cross section set is calculation and/or model independent, and represents the most accurate description of electron interactions with CF_4 that is currently possible from available measurements. From comparison of the calculated and measured swarm parameters the following conclusions are drawn:

(1) The agreement between measured swarm parameters and those calculated using the independently assessed cross section set in a multiterm Boltzmann code is generally good, with the exception of the ionization coefficient. This agreement validates both the Boltzmann code as a method of calculating swarm parameters, and the independently assessed cross section set.

(2) The calculated swarm parameters are strongly affected by the cross section for indirect vibrational excitation via the negative ion resonance near 8 eV.

(3) Discrepancies between the measured swarm parameters and those calculated using the independently assessed cross section set may be due to several causes: uncertainties in the cross sections; uncertainties in the measured swarm parameters; the effects of collisions between electrons and excited molecules; and shortcomings of the calculation, such as the inability to address anisotropic scattering and variable energy loses.

(4) The use of independently assessed cross sections, which are not varied in the interative process of the Boltzmann code for the purpose of optimizing agreement between the calculated and measured transport coefficients, avoids the possibility of accepting physically unrealistic cross sections. It also enables a realistic assessment of the physics of electron-collision processes.

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