

1 Addition 3: Re-fitting of I-DI cross sections

The cross sections for the I-DI processes in this present database [1, 2] have been adopted from the earlier data collection [3]. There the following fitting expression was used:

$$\sigma_{ion} = \frac{10^{-13}}{E \cdot I_c} \left[A_1 \ln \left(\frac{E}{I_c} \right) + \sum_{j=2}^N A_j \left(1 - \frac{I_c}{E} \right)^{(j-1)} \right] \quad (cm^2) \quad (1)$$

where I_c has a value close (or equal) to the appearance potential (expressed in eV), E is the collision energy (expressed in eV) and A_j ($j = 1, \dots, N$) are fitting parameters. The number of fitting parameters was determined from the condition that the r.m.s. of the fit is not larger than 2-3%. The term $\ln(E/I_c)$ in expression 1 indicates that dipole-allowed transitions are involved in I-DI processes.

For the total and partial ionization cross sections of the $e + C_xH_y$ ($x = 1, 2, 3; y \leq 2x + 2$) collision systems, the values of I_c and A_j have been given in Table 7 of the report for the Methane family [1], and in Appendix A.1 (Ethane-family) and A.2 (Propane-family), respectively, in the report for the higher hydrocarbons [2].

Expression (1), with appropriate choices of the fitting coefficients A_j , can provide the proper physical behavior in the threshold and asymptotic regions. In contrast to this, for example, the analytic expression used in Ref. [4] have a fixed $(E - E_{th})^2$ behavior in the threshold region, and an exponential decay behavior ($\sim \exp(-aE)$) in the high-energy region (beyond the cross section maximum). Such asymptotic behavior of ionization cross sections is completely un-physical. Of course, also Eq. 1 gives only then correct physical behavior if certain additional conditions for the fitting coefficients are imposed.

In this **addition 3** to the database reports [1, 2] we discuss necessary conditions for the fitting parameters A_j to actually provide the desired physically correct asymptotic behavior, and we correct those of the fits from [1, 2, 3], which due not fulfill these conditions. For convenience we introduce the new independent variable x defined by $x = E/I_c$, so that the fitting function Eq. 1 then reads:

$$F(x) = C \frac{1}{x} \left[A_1 \ln(x) + \sum_{j=2}^N A_j \left(1 - \frac{1}{x} \right)^{(j-1)} \right] \quad (cm^2) \quad (2)$$

with $1.0 \leq x < \infty$ and $C = 10^{-13}/I_c^2$

1.1 Near threshold behavior

Below energies of 20-30 eV, the ionization cross sections considered here are predominantly determined by their threshold behavior,

$$\sigma_{ion} \sim (1 - E_{th}/E)^\alpha \quad \text{for } E_{th,1} \leq E \quad , \quad (3)$$

or, more generally, if more than one reaction channel contributes to a “total” cross section:

$$\begin{aligned} \sigma_{ion} &= d_1 \cdot (1 - E_{th_1}/E)^{\alpha_1} \quad \text{for } E_{th,1} \leq E \leq E_{th,2} \\ & d_1 \cdot (1 - E_{th_1}/E)^{\alpha_1} + d_2 \cdot (1 - E_{th_2}/E)^{\alpha_2} \quad \text{for } E_{th,2} \leq E \\ & \dots \quad . \end{aligned} \quad (4)$$

to account for different internal states (vibrational, rotational, electronic excitation), which can be involved.

The parameter I_C in Eq. 1 plays the role of the threshold energy E_{th} :

$$\sigma_{ion}(E = I_C) = 0$$

and we require, of course:

$$\sigma_{ion}(E) \geq 0 \quad \text{for } I_C \leq E < \infty \quad (5)$$

i.e., $dF(x)/dx \geq 0$ at $x=1$, necessarily.

The Taylor expansion of $f(x)$ at $x = 1$ reads:

$$\begin{aligned} f_{Taylor}(x) &= f(1) + \\ & (A_1 + A_2)(x - 1) + \\ & (-3/2 A_1 - 2 A_2 + A_3)(x - 1)^2 + \\ & (11/6 A_1 + 3 A_2 - 3 A_3 + A_4)(x - 1)^3 + \\ & O((x - 1)^4) \end{aligned} \quad (6)$$

The available experimental total ionization cross sections show that the parameter α determining the near-threshold cross section behavior for this process has the value $\alpha \simeq 3.0$. In view of the similarity of ionization mechanism for all hydrocarbon molecules, it can be safely assumed that the value $\alpha \simeq 3.0$ characterizes the near-threshold cross section behavior also for the other molecules of the methane, ethane and propane families, respectively.

Comparing Eq. 5 and Eq. 6, and with $f(1) = 0$ by definition, we see that, necessarily:

$$\text{Condition Th1: } \quad A_1 + A_2 \geq 0$$

Indeed, all cross section fits from Ref. [3] which violate this condition start, un-physically, with negative values as energy E increases from their threshold parameters I_c . They only return later to positive values and then start to approximate the experimental and or theoretical data.

Because the value of $\alpha \simeq 3.0$ in the near threshold scaling Eq. 3, the first 2 derivatives of $\sigma(E)$ at $E = E_{th}$ can be expected to be zero. We therefore require in the new fits, that also the second derivative near threshold should, at least, be not negative.

$$\text{Condition Th2:} \quad -3/2A_1 - 2A_2 + A_3 \geq 0$$

1.2 High energy asymptotic behavior

As pointed out in [3] the attractive feature of Eq. 1 is that at asymptotically large collision energies it reduces to the Bethe-Born form for the ionization cross section:

$$\sigma_{B-B,i} = \frac{4\pi a_0^2 Ry}{E} M_i^2 \ln(E \cdot C_i), \quad C_i > 0 \quad (7)$$

with some constants M_i (related to the oscillator strength) and C_i , and hence:

$$\sigma_{B-B} = \frac{10^{-13}}{E \cdot I_c} \left[B_1 \ln\left(\frac{E}{I_c}\right) + B_0 \right] \quad (cm^2), \quad B_1 > 0 \quad (8)$$

The asymptotic form of $F(x)$, Eq. 2, reads:

$$F(x)/C = \frac{C}{x} (A_1 \ln(x) + A_2 + A_3 + A_4 + \dots) + O\left(\frac{1}{x^2}\right) \quad (9)$$

with $C > 0$. It follows, that necessarily

$$\text{Condition H1:} \quad A_1 > 0$$

has at least to be fulfilled to provide the proper asymptotic behavior at high energies. One can easily check that all fits in the database [3] with $A_1 < 0$ do, indeed, not have the proper asymptotic behavior, but have, instead, turn negative at some energy E_a and then approach zero from below with a positive slope at high energies.

1.3 New fitting procedure

Based upon the same raw data as in Ref. [3] the fits for all direct ionization and dissociative ionization cross sections have been redone, retaining the fit formula Eq. 1 with $N=6$. The threshold parameter I_c has now been fixed to the threshold energy E_{th} of each reaction as determined either accurately experimentally or from thermochemical tables (previously it was treated as a variable parameter). For the total cross sections, I_c is set to the minimum of all the threshold energies $E_{th,i}$ values for the partial cross sections contributing to the total.

Conditions Th1, Th2 and H1 have then been enforced. In cases in which the raw data did not allow such fits to be obtained, near threshold data have been added before fitting according to

$$\sigma(E) = a \left(1 - \frac{E_{th}}{E}\right)^\alpha, \quad \text{or} \quad (10)$$

$$\sigma(E) = a \left(1 - \frac{E_{th}}{E}\right)^\alpha \frac{1}{E} \ln(e + cE) \quad E_{th} \leq E \leq E_{th}(1 + \epsilon) \quad (11)$$

whichever is more appropriate, with $\alpha = 3$, $c = 0.09$ and with ϵ a small number between 0 and 1 determined by the availability of reliable raw experimental data in the near threshold region.

References

- [1] R. K. Janev and D. Reiter, *Phys. Plasmas* *9*, 4071(2002); see also: R. K. Janev and D. Reiter: "Collision processes of hydrocarbon species in hydrogen plasmas: I. The methane family", Report FZ-Jülich Jül -3966, Forschungszentrum Jülich, Jülich Germany (Feb. 2002).
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- [3] R.K. Janev, J.G. Wang, I. Murakami and T. Kato, "Cross Sections and Rate Coefficients for Electron-Impact Ionisation of Hydrocarbon Molecules", Res. Report NIFS-DATA-68 (2001) (National Institute for Fusion Science, Toki, Japan).
- [4] D. A. Alman, D. N. Ruzic and J.N. Brooks, *Phys. Plasmas* *7*, 1421 (2000)