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# TOTAL IONIZATION CROSS SECTIONS OF MOLECULES BY ELECTRON IMPACT\*

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*Summary:* The theoretical basis for the binary-encounter-Bethe (BEB) model is outlined, and the model is compared to available experiments and other theories for samples of stable molecules, radicals, and positive ions. Possible directions for improving the BEB model are also presented.

## 1. INTRODUCTION

Electron-impact ionization cross sections of atoms and molecules are widely used in many applications such as the modeling of discharge phenomena, plasma processing of materials, fusion plasma modeling, and design of accelerators. Although quantum mechanics was invented almost 80 years ago, we still have not found a reliable theory that can predict ionization cross sections of atoms and molecules of practical interest. During the last decade, theorists finally succeeded in solving the problem of electron-hydrogen atom scattering.<sup>1-3</sup> However, there is no clean *ab initio* theory for ionization cross sections of molecules, even for small, simple molecules such as H<sub>2</sub>. The basic difficulty in developing such a theory is in describing the continuum states of the incident as well as ejected electrons before and after the collision. Hence, most theories for molecular ionization use various levels of approximations and often require empirical parameters, which further limit the applicability of such theories.

The classical theory by Gryzinski<sup>4</sup> does not require empirical parameters, but it works well only on single-orbital molecules such as H<sub>2</sub>. Other models, such as the DM formalism,<sup>5</sup> contain empirical parameters the choice of which is not

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\* Work supported in part by the U.S. Department of Energy, Office of Fusion Sciences.

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always transparent when a user wants to apply the theory to a new class of molecules.

In this article, I will summarize a theory, called the Binary-Encounter-Bethe (BEB) model,<sup>6</sup> which (a) does not contain empirical parameters, (b) offers a simple equation and recipe for the ionization cross section of individual molecular orbitals, and (c) provides reliable cross sections at low as well as high incident electron energies. The BEB model has been verified to produce reliable cross sections for dozens of stable, neutral, large and small molecules (e.g., H<sub>2</sub>, SF<sub>6</sub>), radicals, and singly-charged positive ions.

The theoretical basis for the BEB model is outlined in Sec. 2, the BEB cross sections for ionization of sample molecules, radicals, and ions are compared to existing experiments and other semi-empirical theories in Sec. 3, and unsolved issues and future prospects are listed in Sec. 4.

## 2. THEORETICAL BASIS FOR THE BEB MODEL

Ionizing collisions can be qualitatively divided into two categories; soft and hard collisions. Soft collisions involve small momentum transfers from the incident electron to target bound electrons, and primarily generate slow ejected electrons. Hard collisions involve large momentum transfers and mostly generate fast ejected electrons. This division, however, is only qualitative and hence arbitrary. Roughly two-thirds of total ionization cross sections come from the ejection of slow electrons.<sup>7</sup>

Most collision theories based on quantum mechanics address both types of collisions, a typical one being the Born approximation. An exception is the Mott cross section, which is the exact solution for an idealized problem, namely, the collision of two *free* electrons. The Mott cross section does not include soft collisions arising from the electric dipole (*E1*) interaction between the incident and target electron, while the Born approximation does. The *E1* interaction occurs only for bound electrons.

There have been many attempts in the past by theorists to combine the Mott cross section with the Born cross section because these two theories are the simplest ones based on quantum mechanics. The main hurdle in this approach is the fact that it is *quantitatively* difficult to isolate the part in the Born cross section that is also included in the Mott cross section—i.e., to avoid duplication. This is the primary reason that existing theories of this type had to introduce empirical parameters.

The BEB model overcame this difficulty by requiring the asymptotic forms (high incident electron energy) of the ionization cross section itself and the matching stopping power to satisfy the correct forms predicted by the Born approximation.<sup>6</sup> This requirement produced an equation for differential ionization cross section, i.e., the energy distribution of ejected electrons as a function of the incident electron energy, which we labeled as the binary-

encounter-dipole (BED) model. The total ionization cross section is obtained by integrating the differential ionization cross section over the ejected electron energy.

The BED model uses optical oscillator strengths (OOSs) for individual orbitals as input. The OOSs for individual orbitals, however, are not easy to calculate or measure, except for simple targets such as H, He, and H<sub>2</sub>. To overcome this difficulty, a simplified form of OOS was adopted, and a versatile expression was derived for the total ionization cross section of individual molecular orbitals. This expression is the BEB model, and provides the ionization cross section as a function of the incident electron energy  $T$  for each molecular orbital. The BEB model uses the orbital binding energy  $B$ , orbital kinetic energy  $U$ , and the orbital electron occupation number  $N$ :

$$\sigma_{BEB}(t) = \frac{S}{t + (u + 1)/n} \left[ \frac{\ln t}{2} \left( 1 - \frac{1}{t^2} \right) + 1 - \frac{1}{t} - \frac{\ln t}{t + 1} \right], \quad (1)$$

where  $t=T/B$ ,  $S=4\pi\alpha_0^2 N(R/B)^2$ ,  $u=U/B$ , and  $n$ =principal quantum number of the dominant atomic orbital if  $n > 2$ . For orbitals in  $K$  and  $L$  shells,  $n$  is set to unity. The total ionization cross sections of a molecule is the sum of Eq. (1) for all occupied orbitals of a molecule. The orbital parameters  $B$ ,  $U$ , and  $N$  are readily available from popular molecular wave function codes such as Gaussian and GAMESS.

The first logarithmic term in Eq. (1) comes from the soft collision part of the Born approximation, the rest in the square brackets comes from the Mott cross section. However, the denominator,  $t+(u+1)/n=[T+(U+B)/n]/B$ , is not based on rigorous quantum mechanics. It comes from the binary-encounter theory with the argument that the *effective* energy difference between the incident and target electrons is the incident energy  $T$  plus the potential energy  $B+U$  of the target electron.<sup>8</sup> The kinetic energy becomes high for orbitals with many radial function nodes, and we found it necessary to reduce it for radial functions with many nodes. This is the reason that we introduced the division by  $n$  in Eq. (1) to avoid making the cross section unrealistically small for valence orbitals with many nodes.<sup>9,10</sup> Note that  $t+(u+1)/n$  approaches  $t$  as the incident energy  $T$  increases. The Born approximation is valid at high  $t$ , and it has only  $t$  in the denominator.

For many stable molecules, Eq. (1) has produced total ionization cross sections in excellent agreement both in magnitude (15% or better at the peak) and shape from threshold to several keV in  $T$ . In addition to its simplicity and freedom from adjustable parameters, the BEB model:

- (a) Uses orbital constants specific to a molecule rather than using simple additivity rules based on atoms in a molecule
- (b) Has the correct asymptotic behavior ( $\ln t/t$ ) predicted by the Born approximation, unlike theories based on classical physics
- (c) Applies to stable molecules and radicals of all sizes

- (d) Produces reliable ionization cross sections for singly-charged positive ions by simply replacing  $n$  in Eq. (1) by  $2n$
- (e) Can be applied to atoms essentially in the same form.<sup>11,12</sup>

On the other hand, the BEB model (and its parent BED model) cannot account for:

- (f) Neutral dissociation of the target molecule
- (g) Ionization of negative ions
- (h) Ionization of two or more electrons from the same molecular orbital
- (i) Indirect ionization such as ionization resulting from the excitation of inner-shell electrons (this is known as *excitation-autoionization*)
- (j) Resonances commonly found near ionization thresholds.

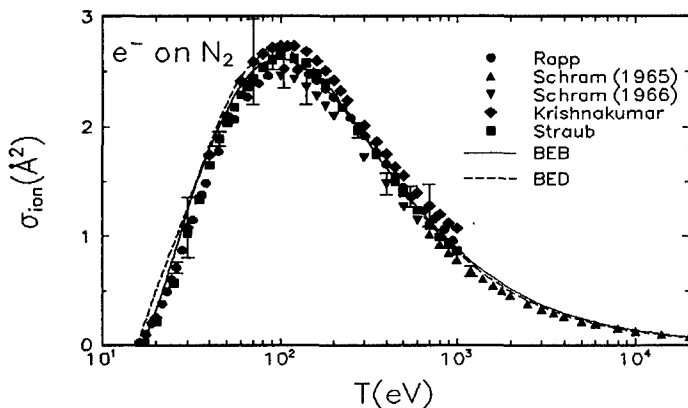
Since the BEB model assumes that an ion is produced whenever the energy transferred to the target exceeds an orbital binding energy, the BEB model overestimates an ionization cross section if neutral dissociation is a significant fraction of the events that follow such an energy transfer. Conversely, if a significant contribution comes from excitation-autoionization, then the BEB model underestimates the ionization cross section.

### 3. COMPARISONS TO EXPERIMENTS AND OTHER THEORIES

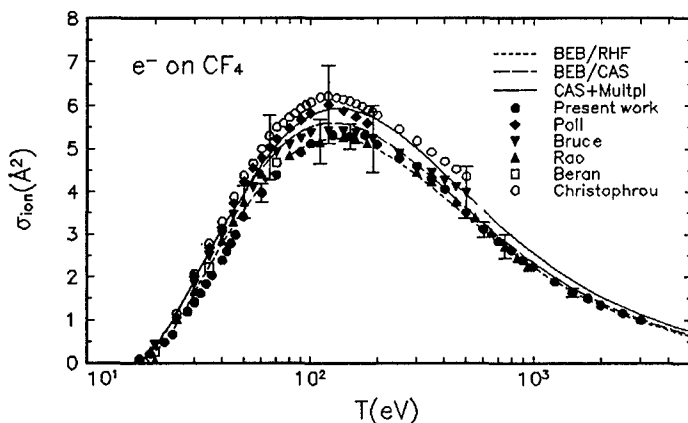
We compare BEB cross sections with available experimental data for  $N_2$ ,  $CF_4$ ,  $SF_6$ ,  $CH_3$ ,  $N_2^+$  and  $SF_5$  in Figs. 1–6. It is clear that the BEB model can produce reliable ionization cross sections for small as well as large, stable molecules. It can also produce reliable cross sections for hydrocarbon radicals and singly-charged positive ions. BEB cross sections of about 90 molecules are available from a public NIST web site.<sup>13</sup>

However, the BEB cross sections calculated from Eq. (1) do not agree well with the experimental data on radicals containing fluorine,  $CF_x$ ,  $SF_x$ , and  $NF_x$ , although the BEB cross sections for the stable molecules  $CF_4$  and  $SF_6$  agree well with experiments.

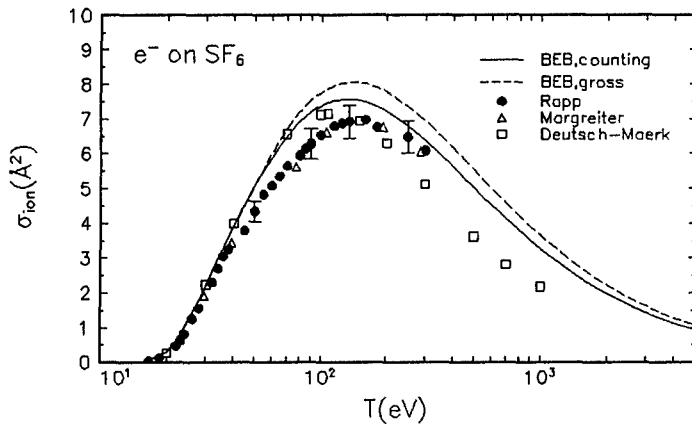
Huo has modified the BED model by replacing the first logarithmic term in Eq. (1), which represents the  $E1$  interaction, with the Born cross section.<sup>19–21</sup> Her model is called a *simplified version of the improved BED*, or siBED model. She replaced the  $E1$  interaction term with her version of the full Born cross section, which contains two adjustable parameters and a generic OOS more elaborate than the one used in the BEB model. Although the thorny issue of avoiding the duplication of hard collisions contained both in the Born and Mott cross sections has not been addressed directly by Huo, presumably it is solved by setting two adjustable parameters in the model to reproduce well known cross sections of other molecules. The siBED cross sections are in excellent agreement with the experimental data on  $CF_x$ ,  $NF_x$ , and  $SF_x$ .



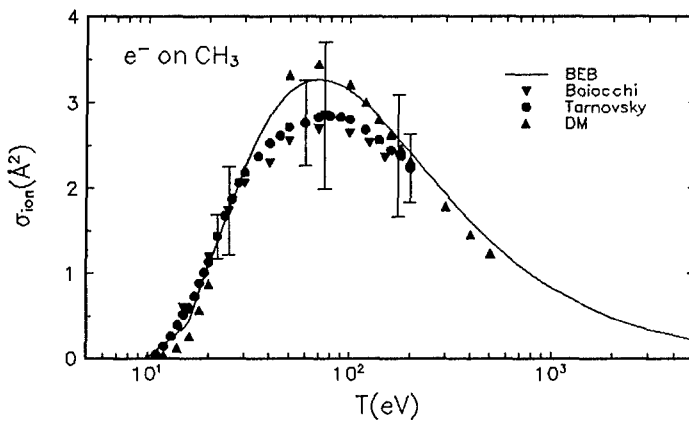
**Figure 1.** Total ionization cross section of  $N_2$  (from Fig. 2 of Ref. 14). Solid symbols are experimental data. Optical oscillator strengths needed for the BED model was deduced from photoionization experiments.



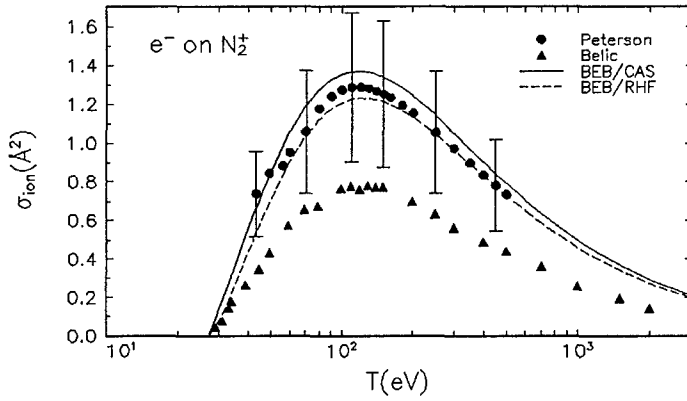
**Figure 2.** Total ionization cross section of  $CF_4$  (from Fig. 4 of Ref. 15). RHF=restricted Hartree-Fock (uncorrelated) wave function, CAS=complete active space (correlated) wave function, Multipl=includes multiple ionization, solid circle=experiment by Nishimura (Ref. 15), open circle=recommended cross section by Christophrou and Olthoff, other symbols are experimental data.



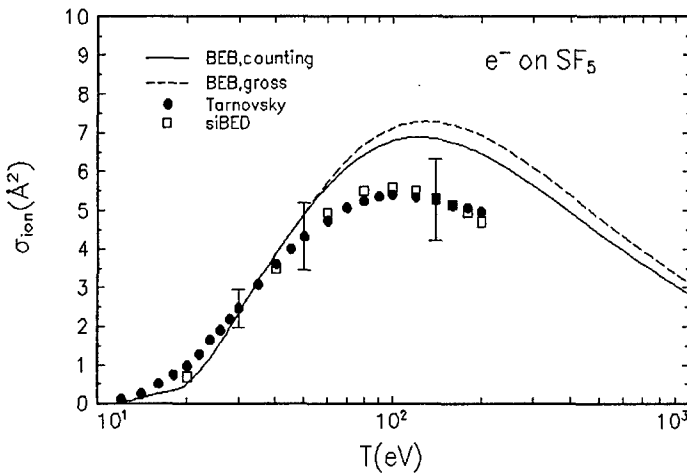
**Figure 3.** Total ionization cross section of  $\text{SF}_6$  (adapted from Fig. 1 of Ref. 16). Rapp=experimental absolute cross section, Margreiter=relative cross section normalized to Rapp, Deutsch-Märk=DM formalism (Ref. 5).



**Figure 4.** Total ionization cross section of  $\text{CH}_3$  (from Fig. 5 of Ref. 17). DM=DM formalism (Ref. 5), other symbols are experimental data.



**Figure 5.** Total ionization cross section of  $\text{N}_2^+$  (from Fig. 2 of Ref. 18). Symbols are experimental data. See caption of Fig. 2 for CAS, RHF.



**Figure 6.** Total ionization cross section of  $\text{SF}_5$  (adapted from Fig. 2 of Ref. 16). Tarnovsky=experiment, siBED=new model by Huo (Ref. 21).



Neutral dissociation amounts to about 20% of the total ionization cross section in  $\text{CF}_4$ .<sup>22</sup> We found that the difference between the experimental ionization cross section measured by Nishimura<sup>15</sup> and the BEB cross section<sup>15</sup> closely follows the shape of the measured cross section for the neutral dissociation,<sup>15</sup> strongly indicating that about one-half of the neutral dissociation comes from energy transfers exceeding the ionization energy of  $\text{CF}_4$ . The other half presumably resulted from energy transfers less than the ionization energy. The magnitudes of neutral dissociation in  $\text{CF}_x$ ,  $\text{NF}_x$ , and  $\text{SF}_x$  are unknown.

#### 4. CONCLUSIONS AND FUTURE OUTLOOK

The BEB model has demonstrated its versatility in providing reliable total ionization cross sections for a wide range of molecules, large and small, including radicals and positive ions. The formula and procedure to use for the model are simple enough that anyone who has access to popular quantum chemistry codes can produce the necessary molecular orbital constants and calculate the desired ionization cross sections. For many molecules, ionization cross sections are readily available from the NIST web site,<sup>13</sup> which is updated as new BEB cross sections become available. The web site also offers instantaneous on-line calculations of total ionization cross sections of the molecules included in the web site by simply typing in the incident electron energy.

Huo has offered an improved version of the BED (siBED) model.<sup>19-21</sup> Her siBED model is not as simple to use as the original BED/BEB model, and it has been tested mostly on fluorine-containing radicals, after adjusting two empirical parameters in the model to known cross sections of other stable molecules. It is desirable to establish the versatility of the model and the universality of the empirical parameters in the model by applying it further to a wider range of molecules.

As for the present BEB model, we have begun to explore the possibility of accounting for the excitation-autoionization (EA) using a new scaling method, which turned out to be very successful in atoms. For electric dipole ( $E1$ ) and spin allowed excitations in atoms, it was found that the plane-wave Born (PWB) excitation cross sections were converted to accurate cross sections by the following scaling:

$$\sigma_{BE}(T) = \frac{T}{T + B + E} \sigma_{PWB}(T), \quad (2)$$

where  $E$ =excitation energy. This scaling is called the BE scaling,<sup>23</sup> and it has been verified for discrete excitations of many neutral atoms, hydrogen through thallium. For singly-charged positive ions of atoms, a similar scaling converted Coulomb-Born (CB) excitation cross sections into accurate cross sections:

$$\sigma_E(T) = \frac{T}{T + E} \sigma_{CB}(T). \quad (3)$$

This scaling is called the E scaling.<sup>24</sup> The BE and E scaling methods provide easy and efficient ways to calculate accurate excitation cross sections not only for the excitations to bound excited states, but also to the core-excited, autoionizing states, which are extremely difficult to calculate with conventional theories such as the R-matrix and close-coupling methods. We have used these two scaling methods to reveal that almost one-half of the total ionization cross sections of Al, Ga, and In come from excitation-autoionization.<sup>11</sup>

For almost all neutral atoms, the BEB model alone was insufficient to account for total ionization cross sections because of the contributions from EA, which is not included in the BEB model. The fact that the BEB model has been very successful on so many molecules indicates that EA may not play a significant role in molecules. Core-excited states in molecules may preferably lead to neutral dissociation. This is a worthwhile subject to pursue.

On the other hand, comparisons of BEB ionization cross sections of CS and S<sub>2</sub> with available experiments<sup>25</sup> strongly suggest that the contribution from EA is significant. A similar situation also exists for OH. Our preliminary study indicates that the E scaling may convert PWB cross sections to reliable ones for the excitation of neutral molecules by electron impact. If the applicability of the E scaling—or a variation of it—to neutral molecules is verified, then not only we can get accurate cross sections for excitations to bound excited states, but also we can accurately predict the contribution to total ionization cross sections through excitations of core electrons to autoionizing states.

## 5. ACKNOWLEDGEMENTS

The author is grateful to Dr. W. M Huo for providing her results on SF<sub>x</sub> prior to publication, and to Prof. M. A. Ali and Dr. K. K. Irikura for generating ionization cross sections of many molecules and enlightening discussions of molecular properties.

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