Performance of binary-encounter-Bethe (BEB) theory for electron-impact ionization cross sections of molecules containing heavy elements ($Z > 10$)

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The binary-encounter-Bethe (BEB) theory developed by Kim and coworkers has been successful for computing electron-impact ionization cross sections of many molecules. However, some recent publications have stated that BEB theory performs poorly for molecules that contain heavier elements such as chlorine and sulfur. We have found that the BEB calculations in those publications were performed incorrectly. When performed correctly, BEB predictions are as good for heavy-element molecules as for light-element molecules. We recommended recently that an alternative, less-confusing procedure be used for molecules that contain heavier elements. The alternative procedure, based upon effective core potentials (ECPs), does not require explicit kinetic energy corrections. For peak cross sections of a group of 18 molecules, the root-mean-square difference between BEB predictions and experimental values is 13%. Results are presented for CCl_3CN, C_2Cl_6, C_2HCl_5, C_2Cl_4, both isomers of $C_2H_2Cl_4$, CCl_4, $TiCl_4$, CBr_4, $CHBr_3$, CH_2Br_2, GaCl, CS_2, H_2S, CH_3I, $Al(CH_3)_3$, $Ga(CH_3)_3$, and hexamethyldisiloxane. Incorrect BEB calculations have been reported in the literature for several of these molecules.

KEYWORDS: *ab initio*; cross section; electron impact; ionization; molecule; theory

INTRODUCTION

Electron-impact ionization cross sections are essential quantities for modeling a variety of important processes. For example, low-temperature plasmas are important in semiconductor processing and in the destruction of volatile organic compounds. Low-temperature plasmas also modify the mechanical properties of surfaces, both intentionally, in materials processing, and unintentionally, in nuclear fusion reactors. Absolute ionization cross sections are also needed for obtaining quantitative gas densities from mass-spectrometric measurements. Examples are flame sampling and Knudsen-cell mass spectrometry.

Unfortunately, absolute ionization cross sections are difficult to measure precisely. Even for convenient, stable molecules, experimental groups often disagree significantly on the values of the cross sections.[1] Furthermore, many of the interesting cross sections are for molecules that are especially difficult to measure, such as free radicals and molecular ions. Thus, reliable theoretical predictions are valuable.

The binary-encounter-Bethe (BEB) model2 [3] has been shown to produce reliable cross sections for many systems for which experimental data are available.[4] However, there have been some reports that its predictions are as much as 45% too low for molecules that contain heavier elements (atomic number $Z > 10$). The purposes of the present paper are (1) to determine the origin of these serious apparent discrepancies and (2) to evaluate the performance of the simplest appropriate version of BEB theory.

THEORETICAL PROCEDURES

BEB theory predicts the ionization cross section for each canonical molecular orbital (MO) as a function of the incident electron energy, T. The total cross section is the sum of the cross sections for the individual MOs, given by

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

where $t = T/B$, $u = U/B$, $S = 4\pi a^2_0 N(R/B)^2$, a_0 is the Bohr radius, and R is the Rydberg energy. B, U, and N are the binding energy (i.e. the vertical ionization energy), the kinetic energy, and the occupation number, respectively, for the MO. When $T < B$, the MO cannot be ionized, so $\sigma_{MO} = 0$. The constant n is a scaling factor whose role will be discussed below. When B exceeds the second ionization energy (IE_2), the molecule will presumably become doubly charged through an Auger process. In that case, the contribution of σ_{MO} is doubled to correspond to experimental measurements of ion current (i.e. gross ionization cross section).

For a neutral molecule composed only of light atoms ($Z < 10$), Eqn (1) is used with $n = 1$ for all orbitals. When molecules contain heavy atoms, there are two alternatives for applying the BEB model to the valence orbitals.

In the first method,[5] all electrons are included explicitly in the *ab initio* calculations. For each MO, the scaling factor n in Eqn (1) is unity unless the orbital is dominated by atomic orbitals with principal quantum number >2, as judged by a Mulliken population >50%. When this is the case, n is set equal to the principal quantum number of the dominant atomic orbitals. Although the 50% threshold is rather arbitrary, choosing a different value generally changes the peak molecular cross section by less than 10%.[1]

In the second method,[6] the core electrons of the heavy atoms are replaced by effective potentials (effective core potentials (ECPs)). The resulting valence pseudo-orbitals lack the inner radial nodes of normal orbitals and so their kinetic energies are much lower than normal. Thus, Eqn (1) is used with $n = 1$ for all valence MOs. No Mulliken populations are needed. However, since many core orbitals are missing in an ECP calculation, their contribution to the ionization cross section can only be obtained from a separate, all-electron calculation. This ECP method is recommended over the all-electron method for molecules that contain heavier atoms ($Z > 10$).[7] Consequently, only the performance of the ECP method is evaluated in the present study.

COMPUTATIONAL METHODS

All *ab initio* calculations were performed with the Gaussian 03 program suite using basis sets as implemented therein.[8] Basis sets listed in square brackets were used on centers with $Z > 36$ (that is, beyond Kr). Molecular geometries were computed using the B3LYP (Becke three-parameter exchange with Lee-Yang-Parr correlation) hybrid density functional[9,10] with the 6-31G(d) [3-21G(d)] basis sets, with all electrons explicit. Vibrational frequencies were computed to verify that all structures were energy minima. These geometries were used for all subsequent calculations.

Binding energies, *B*, kinetic energies, *U*, and Mulliken populations were computed at the Hartree–Fock (HF) level using the 6-311G(d,p) [3-21G(d)] basis sets. These are all-electron basis sets, which are needed to obtain the contributions from the core orbitals on heavy atoms. For pseudopotential calculations, the Stuttgart quasi-relativistic ECPs and corresponding valence 'MWB' (neutral-optimized, quasi-relativistic Wood-Boring) basis sets were used on heavy atoms.[11,12] A set of *d* polarization functions, taken from the corresponding 6-311G(d,p) [3-21G(d)] all-electron basis, was added to each heavy center. This combination of ECP, MWB basis, and polarization set is labeled as ECP(d) here.

The BEB ionization cross section is sensitive to the vertical ionization energy of the molecule (i.e. the ionization threshold). Koopmans (i.e. HF) binding energies are too approximate for this purpose. More accurate values of *B* for the valence orbitals were computed using the outer-valence Green's function (OVGF) method[13,14] with the 6-311 + G(d,p) [3-21G(d)] basis sets. For the chlorofluoromethanes, the binding energies from this procedure are lower than corresponding experimental values by only 0.3 eV.[1] OVGF results were rejected for pole strengths < 0.75. When available, experimental vertical ionization energies were used for the outermost valence orbitals.

Ionization of deeper orbitals can lead to double ionization through an Auger mechanism. For comparison with cross-section measurements based on ion current, the contributions from these

orbitals are doubled. Second ionization energies, IE_2, were taken either from experiment or from B3LYP/6 311G(d,p) [ECP(d)] calculations at the geometry of the neutral molecule, considering both singlet and triplet dications.

We attempted to reproduce the poor BEB results published previously. Since details were not provided, we performed simplified, all-electron BEB calculations. Geometries were computed at the HF/6-31G(d) level. Koopmans' binding energies and kinetic energies were from HF/6-311G(d,p) single-point calculations. Double ionization was neglected.

RESULTS

We selected a representative set of molecules for which total ionization cross sections have been measured experimentally and which contain heavy atoms. For computational convenience, only closed-shell molecules were considered. Along with references for the experimental cross sections, the molecules are: C_2Cl_6, C_2HCl_5, C_2Cl_4, 1,1,1,2-$C_2H_2Cl_4$, and 1,1,2,2-$C_2H_2Cl_4$;[15] CCl_4;[15,16] $TiCl_4$;[17] CCl_3CN, CBr_4, $CHBr_3$, and CH_2Br_2;[18] GaCl;[19] CS_2;[20–22] H_2S;[21,23,24] CH_3I;[25,26] $Al(CH_3)_3$ and $Ga(CH_3)_3$;[27] and hexamethyldisiloxane (TMS_2O).[28]

Tables of MO data used to generate the BEB cross sections are available from the authors upon request. As mentioned above, some vertical ionization energies[29–36] and double-ionization energies[37–41] were taken from experimental measurements. In a few cases, the theoretical results led us to reassign the experimental photoelectron spectra.

Claims of poor BEB performance

We examined several of the cases in which BEB predictions were claimed to lie far below the experimentally determined values for peak ionization cross sections.[15,18,22,25] All the BEB calculations so reported were computed using the all-electron version of BEB theory, in which the $1/n$ factor in the denominator of Eqn (1) is important. None of the MO parameters were reported,[15,18,22,25] so we have calculated them anew for this study. Since our goal is to mimic the published calculations, we performed simplified all-electron BEB calculations as described in the

‘Computational Methods’ section. These are cruder than the calculations that we have used elsewhere.[7]

The ‘Expt’ and ‘Poor BEB’ columns of Table 1 list the experimental and published BEB values of the peak ionization cross sections for several molecules for which BEB theory was claimed to work poorly.[15,18,22] For this group of molecules, published BEB values are an average of 39% lower than the corresponding experimental values.

We attempted to reproduce these poor BEB results. However, even the crude all-electron calculations worked much better than the published claims, differing from the experimental values by only -9% (mean). BEB peak cross sections from our crude all-electron calculations are included in Table 1 (‘Crude BEB’ column). If we (incorrectly) omit the factor of $1/n$ in the denominator of Eqn (1), we obtain good agreement with the earlier, poor results. These intentionally incorrect values are listed in the ‘Incorrect BEB’ column of Table 1. On average, they are 40% lower than the corresponding experimental values.

Performance of recommended BEB theory for molecules containing ‘heavy’ elements

The simplest comparison between theoretical and experimental cross sections is the peak value. Table 2 lists the peak cross sections from experimental measurements and from BEB calculations (using the ECP procedure described in the ‘Computational Methods’ section). The average reported experimental uncertainty is 6%. The average difference between the theoretical and experimental peak cross sections is -2%, including all available experimental measurements. On a root-mean-square basis, theory differs from experiment by 13%. The largest discrepancies are for H_2S, $Ga(CH_3)_3$, and CS_2. For H_2S, the theory deviates from the three experimental measurements by -27%, +17%, and -17%.[21,23,24] For CS2, the discrepancies are +6%, +4%, and -20%.[20–22] For $Ga(CH_3)_3$ theory is 24% higher than the lone experiment, but there may be some difficulty with the experimental cross section, which is smaller for $Ga(CH_3)_3$ than for the lighter analogue $Al(CH_3)_3$.[27]

Graphical comparisons of BEB results with experimental measurements are provided in Figs 1 and 2 for the 'problem' molecules H_2S and CS_2, respectively. Figure 3 shows the comparison for a bromine-containing molecule, CH_2Br_2. Figure 4 is for both isomers (1,1,1,2- and 1,1,2,2-) of tetrachloroethane.

[Insert Table 1 and 2 and Figure 1]

DISCUSSION

As shown by the results in Table 1, the earlier calculations erred by neglecting the factor of $1/n$ in Eqn (1). This was not because the factor was omitted from consideration, but because of software problems that nullified its effect.[42] This led to serious discrepancies with experimental data, resulting in the erroneous conclusion that BEB theory performs poorly for molecules that contain heavier elements ($Z > 10$).[15,18,22,25] The good results obtained using a correct, but still crude, all-electron calculation, show that all-electron BEB theory provides reliable predictions even for such molecules. This is consistent with our previous, good results for the chlorofluoromethanes and other molecules containing heavier elements.[1,7]

[Insert Figures 2, 3 and 4]

Table 2 shows good performance for the BEB theory, obtained using the ECP procedure described in the 'Computational Methods' section, as recommended elsewhere.[7] The root-mean-square difference between theory and experiment, including experimental data that disagree with each other, is only 13%. The figures compare theoretical and experimental cross sections at energies besides the peak. The poorest agreement is obtained for H_2S (Fig. 1). We have no explanation for the disagreement. However, we note that autoionization is sometimes significant, at least for atoms,[43–45] and that there is substantial disagreement among the three experiments.

The second-worst disagreement between BEB theory and repeated experiment is for CS_2 (Fig. 2). However, the strong disagreement is only with the measurements by Hudson *et al.*[22]

The peak BEB cross section agrees well with that by Rao and Srivastava,[20] but theory does not predict the unusual double peak found only in that experiment. The BEB values agree well with the measurements by Lindsay *et al.*[21] across the energy range.

Figure 3 shows results for CH_2Br_2, which has been reported to be problematic for BEB theory.[18] In contrast to the earlier results, we find fairly good agreement between theory and experiment. Likewise, the BEB results agree with experimental measurements[15] for 1,1,2,2-tetrachloroethane (Fig. 4). For the 1,1,1,2-isomer, agreement is only within 15%. BEB theory predicts the two isomers to have the same cross section (within 2%), while the experiment found a noticeably larger cross section for the asymmetric isomer.

The ECP procedure still requires performing all-electron calculations to obtain cross sections for the core orbitals. This is cumbersome for molecules containing very heavy atoms that lack good all-electron basis sets. Alternatively, binding and kinetic energies for the core orbitals can be taken from atomic calculations,[6] independent of the particular molecule at hand. For the molecules examined here, completely ignoring the contribution of the core by using ECPs for all calculations reduced the cross section by only a small percentage, particularly at energies below 100 eV. Thus, if the energies of interest are not too high, the core can be neglected entirely and no all-electron calculations are needed at all. This is the usual situation in applications such as mass spectrometry.

CONCLUSIONS

BEB theory successfully predicts total cross sections for electron-impact ionization of molecules, whether the molecules contain heavier elements ($Z > 10$) or not. The present results were obtained using the ECP method of calculation, which is easier to execute than the original, all-electron method.

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Table 1. Peak total ionization cross sections in $Å^2$

was reported to perform poorly.[15,16,22]
are described in the text

Molecul	Expt.	Poor BEB	BEB	C BEB
CS2	11.70[22]	6.50[22]	6.6	9.6
CH2Br	11.67[16]	7.76[16]	7.4	11.6
CHBr3	13.75[16]	9.86[16]	9.3	14.9
CCl4	15.45[15]	9.76[15]	9.9	14.8
C2Cl4	21.74[15]	11.3[15]	11.4	16.6
C2Cl6	26.61[15]	15.10[15]	15.3	22.9

Table 2. Experimental and calculated peak total ionization cross sections in $Å^2$ (1 $Å^2$ = 10^{-20} m^2)

Molecule	Expt.	BEB (TCB)
CCl3CN	14.11 f 0.56[18]	15.0
C2Cl6	26.61 f 1.06[15]	24.7
C2HCl5	23.61 f 0.94[15]	21.6
C2Cl4	21.74 f 0.87[15]	17.8
1,1,1,2-	21.24 f 0.85[15]	18.4
1,1,2,2-	19.66 f 0.79[15]	18.8
CCl4	15.45 f 0.62,[15] 15.15 f	15.6
TiCl4	16.45 f 2.47[17]	17.5
CBr4	19.0 f 0.76[16]	19.7
CHBr3	13.75 f 0.55[16]	14.9
CH2Br2	11.67 f 0.47[16]	11.4
GaCl	9.25 f 0.93[19]	8.3
CS2	9.03 f 0.54,[21] 11.70 f 8.85 f 1.33[20]	9.4
H2S	3.93 f 0.51,[24] 5.53 f 6.28[23]	4.6
CH3I	10.3 f 0.3,[25] 9.64 f 0.58[26]	8.7
Al(CH3)3	13 f 127,a	14.4
Ga(CH3)3	12 f 127,a	15.7
TMS2O	26.41 f 3.96[26,b]	28.6

a At 70 eV, not necessarily the peak.
b At 100 eV, not necessarily the peak.

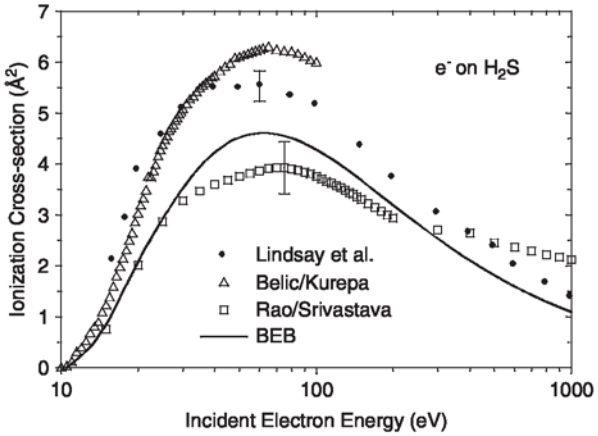

Figure 1. Total ionization cross section for H_2S. Experimental values are indicated by the symbols.[21,23,24] Theoretical (BEB-ECP) values are indicated by the curve.

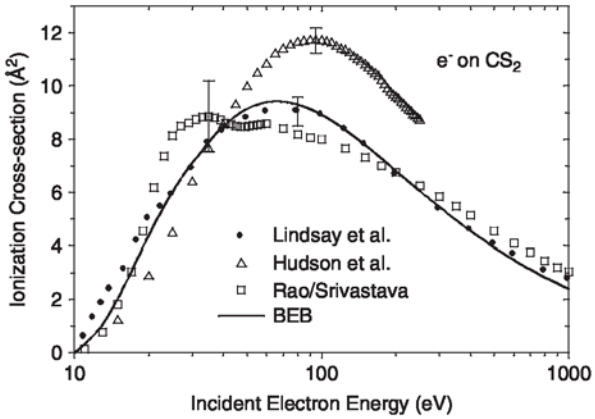

Figure 2. Total ionization cross section for CS_2. Experimental values are indicated by the symbols.[20–22] Theoretical (BEB-ECP) values are indicated by the curve.

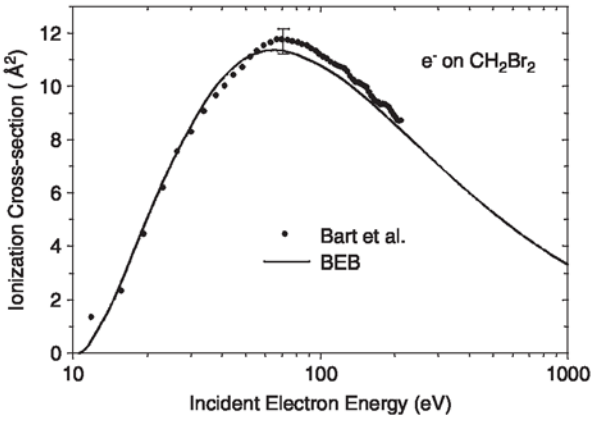

Figure 3. Total ionization cross section for CH_2Br_2. Experimental values are indicated by the symbols.[18] Theoretical (BEB-ECP) values are indicated by the curve.

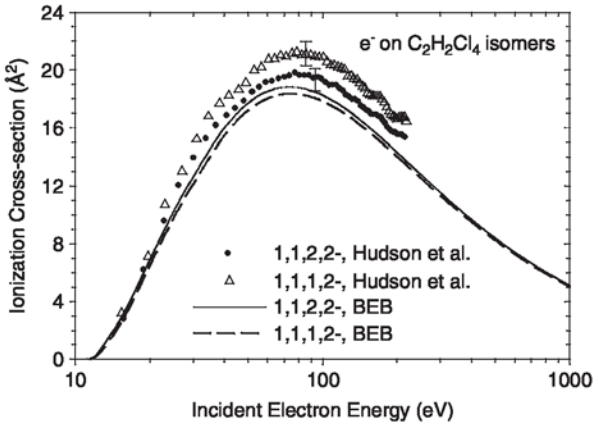

Figure 4. Total ionization cross section for 1,1,1,2- and 1,1,2,2-tetrachloroethane, $C_2H_2Cl_4$. Experimental values are indicated by the symbols.[15] Theoretical (BEB-ECP) values are indicated by the curves.