**Test of the Validity of Bragg´s Rule for Mean Excitation Energies**

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***Abstract***

We are investigated the effect of chemical binding on the validity of Bragg’s rule for the calculation of stopping cross sections and mean excitation energies. As test cases we use a series of small molecules and molecular ions, primarily carbon and nitrogen halides. We find that neglect of chemical binding nearly always reduces the mean excitation energies and that the fully atomic decomposition of any molecule but a diatomic molecule never gives the best fulfilment of Bragg’s rule. The best fulfilment of Bragg’s rule is obtained when as few bonds as possible are broken and when the choice of fragments is guided by chemical knowledge. By investigating several alternative fragmentation patterns for a molecule, guidelines for choice of optimal fragmentation are suggested.

***Keywords:*** Stopping cross sections, Bragg’s rule, mean excitation energies, radiation physics, health physics, radiation dosimetry, small molecules

1. **Introduction**

Additivity of energy loss is one of the most powerful tools in predicting the stopping power of large compounds or mixtures of compounds from their constituents. It has been widely used in fields where stopping power of complex targets are needed, including radiation dosimetry, plasma physics, and radiation physics and chemistry. At intermediate to high projectile energies accuracies of 2 to 3 % of the stopping power can be achieved using this method [1]. The additivity was predicted by Bragg and Kleeman in 1905 [2] and has since been referred to as Bragg’s rule of stopping power additivity.

Bragg´s rule assumes that the stopping power of a mixture is the weighted sum of the stopping power of the individual components. It is thus disregarding phase effects and when applied to the calculation of stopping power of a molecule from its atomic or molecular constituents it is neglecting the effects of chemical binding. Phase effects on the validity of Bragg’s rule can be eliminated when comparing stopping power data for the compound and its fragments in the same phase. Thus, comparing stopping power data for molecules and their constituent atoms in the gas phase can be used to get an estimate of the binding effects on the fulfilment of Bragg’s rule. That was first done by Zeiss *et al.* [3] for a few small, neutral molecules that were decomposed into their atomic constituents and for which they were able to determine the individual mean excitation energies with a range of methods.

In this communication we are extending this study also to include other fragments than the pure atomic fragments and we are investigating the fulfilment of Bragg’s rule for a larger group of molecules, including molecular ions. Also, we are using mean excitation energies for both the compound molecule or ion and its constituents obtained with precisely the same theoretical method and we thus have a pure test of the validity of Bragg’s rule itself for the selected group of molecules and molecular ions.

1. **Method**

Bragg’s rule [2] states that

 (1)

where is the stopping cross section of a compound or molecule consisting of *N* fragments with individual stopping cross sections , is the number of electrons in the compound, the velocity of the incoming projectile, and

 (2)

For sufficiently fast projectiles, *e.g.* MeV protons, the bulk of the stopping cross section is determined by the Bethe [4] formula

 (3)

where *Z1* and *Z2* are the projectile charge and target electron number, respectively. The mean excitation in Eq. (3) is defined through the relation

 (4)

Here, is the excitation energy between the ground state and the excited state and is the corresponding dipole oscillator strength. The summation in Eq. (4) extends over all excited states and it should in principle have been integration over the continuum states. However, in finite basis set calculations as the present this integration is replaced by a summation over a finite number of pseudo-states placed in the continuum. We know [5] that this gives a good representation of the continuum contributions to sum over states properties as the one in Eq. (4), provided large and flexible basis set are used and all excitations in basis set are included in the sum over states expressions.

Inserting Eq. (3) in Eq. (1) we find that

 (5)

which we may refer to as Bragg’s rule for mean excitation energies. It gives an estimate the mean excitation energy of a compound from the mean excitation energies of the constituents of the compound

The main purpose of this paper is to investigate how well Eq. (5) works for a few small molecules and molecular ions depending on how they are divided up into fragments. For all molecules, ions and atoms the gas phase mean excitation energies are calculated in Random Phase Approximation (RPA) [6] using the aug-cc-pCV5Z basis set, i.e. applying the same methodology for all involved atoms and molecules. We make use of some recently published mean excitation energies for molecular ions [7] and atoms and their ions [8,9]. We will report new values for a few new molecules obtained using the same RPA method and the same one-electron basis set.

In the next sections we will test the validity of Eq. (5) for selected molecules and molecular ions.

1. **Results**

In Tables 1-3 we have listed the mean excitation energies calculated for molecules and molecular ions and compared them to various ways of braking the molecule or molecular ion up into fragments. The second column lists the directly calculated RPA values for the molecules. The fourth column lists the mean excitation energies for the same molecule as obtained using Bragg’s rule in Eq. (5) and the fragmentations described in column 3. The last column gives the absolute and per cent difference between the directly calculated I0 and the one obtained applying Eq. (5).

For each molecule the entries are organized in descending order of agreement between the directly calculated molecular mean excitation energies and the one obtained using Bragg’s rule.

Table 1. Comparison of molecular, RPA mean excitation energiesa (in eV) with those obtained using Bragg’s rule in Eq. (5) and I0i from [8-9] for the atomic and ionic fragments.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Molecule/ion  | I0 from [7] | Fragmentsc | I0 from Eq. (5) | ΔI0d(in %e)f |
| H2+ | 18.6b | H + H+ | 15.0 | -3.6(-19.4)\* |
|  |  |  |  |  |
| H3 | 16.5 | H2 + H | 17.9 | 1.4(8.5)\* |
| H3 | 16.5 | 3H | 15.0 | -1.5(-9.1) |
| H3 | 16.5 | H2+ + H- | 9.4 | -6.9(-41.8) |
|  |  |  |  |  |
| H3+ | 20.9 | H2 + H+ | 19.5 | -1.4(-6.7)\* |
| H3+ | 20.9 | H2+ + H | 16.7 | -4.2(20.1) |
| H3+ | 20.9 | 2H + H+ | 15.0 | -5.9(-28.2) |
|  |  |  |  |  |
| C2 | 69.8 | C + C | 65.9 | -3.9(-5.6)\* |
| C2 | 69.8 | C+ + C- | 60.7  | -9.1(-13.0)  |
|  |  |  |  |  |
| C2- | 56.9 | C + C- | 53.6 | -3.3(-5.8)\* |
|  |  |  |  |  |
| CN | 76.3 | C + N | 73.9 | -2.4(-3.1)\* |
| CN | 76.3 | C+ + N- | 69.1 | -7.2(-9.4) |
| CN | 76.3 | C- + N+ | 67.2 | -9.1(-11.9) |
|  |  |  |  |  |
| CN- | 64.4 | C + N- | 61.0 | -3.4(-5.3)\* |
| CN- | 64.4 | C- + N | 60.5 | -3.9(-6.1)  |
|  |  |  |  |  |
| OH | 82.4 | O + H | 79.5 | -2.9(-3.5)\* |
| OH | 82.4 | O- + H+ | 73.5 | -8.9(-10.8) |
| OH | 82.4 | O+ + H- | 65.3 | -17.1(-20.8) |
|  |  |  |  |  |
| OH- | 65.0 | O- + H | 62.7 | -2.3(-3.5)\* |
| OH- | 65.0 | O + H- | 57.3 | -7.7(-11.8) |
|  |  |  |  |  |
| OH+ | 100.2 | O + H+ | 97.9 | -2.3(-2.3)\* |
| OH+ | 100.2 | O+ + H | 96.0 | -4.2(-4.2) |

a Unless otherwise indicated the molecular mean excitation energies are taken from Table 1 of [7].

b I0(H2+) = 18.59 eV. It is calculated using the method of [7] at a bond length of 1.05716 Å.

c I0(H2) = 19.47 eV [10]. It is calculated using the method of [7].

d ΔI0 is defined as column 4 minus column 2.

e Calculated as ΔI0/I0 in %.

f The asterisk indicates the composition for which we find the best agreement between the directly calculated mean excitation energy and the one obtained using Bragg’s rule.

Table 2. Comparison of molecular, RPA mean excitation energies (in eV) of carbon hydride molecules and molecular ions from Table 2 of [7] with those obtained using Bragg’s rule in Eq. (5) and I0i from [8-9] for the atomic fragments and from [7,10] for the molecular fragments.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Molecule/ion | I0 from [7] | fragments | I0 from Eq. (5) | ΔI0a(in %b)c |
| CH | 56.1 | C + H | 53.3 | -2.8(-5.0)\* |
| CH | 56.1 | C- + H+ | 44.9 | -11.2(-20.0) |
| CH | 56.1 | C+ + H- | 43.7 | -12.4(-22.1) |
|  |  |  |  |  |
| CH+ | 71.8 | C+ + H | 68.4 | -3.4(-4.7)\* |
| CH+ | 71.8 | C + H+ | 65.9 | -5.9(-8.2) |
| CH+ | 71.8 | C2+ + H- | 49.6 | -22.2(-30.9) |
|  |  |  |  |  |
| CH2 | 50.9 | C +H2 | 48.6 | -2.3(-4.5)\* |
| CH2 | 50.9 | CH + H | 47.6 | -3.3(-6.5) |
| CH2 | 50.9 | C + 2H  | 45.5 | -5.4(-10.6) |
| CH2 | 50.9 | C- + H2+ | 40.2 | -10.7(-21.0) |
| CH2 | 50.9 | C+ + H- + H | 38.3 | -12.6(-24.8) |
| CH2 | 50.9 | C2+ + 2H-  | 30.1 | -20.8(-40.9) |
|  |  |  |  |  |
| CH2+ | 62.7 | C+ + H2 | 59.3 | -3.4(-5.4)\* |
| CH2+ | 62.7 | CH+ + H | 57.4 | -5.3(-8.5) |
| CH2+ | 62.7 | CH + H+ | 56.1 | -6.6(-10.5) |
| CH2+ | 62.7 | C++2H | 55.0 | -7.7(-12.3) |
| CH2+ | 62.7 | C + H2+ | 55.0 | -7.7(-12.3) |
| CH2+ | 62.7 | C + H + H+ | 53.3 | -9.4(-15.0) |
| CH2+ | 62.7 | C- + 2H+ | 44.9 | -17.8(-28.4) |
| CH2+ | 62.7 | C2+ + H- + H | 41.8  | -20.9(-33.3) |
|  |  |  |  |  |
| CH22+ | 75.3 | CH+ + H+ | 71.8 | -3.5(-4.6)\* |
| CH22+ | 75.3 | C+ + H2+ | 70.9 | -4.4(-5.8) |
| CH22+ | 75.3 | C2+ + H2 | 70.8 | -4.5(-6.0) |
| CH22+ | 75.3 | C+ + H + H+ | 68.4 | -6.9(-9.2) |
| CH22+ | 75.3 | C + 2H+  | 65.9 | -9.4(-12.5) |
| CH22+ | 75.3 | C2+ + 2H | 64.8 | -10.5(-13.9) |
|  |  |  |  |  |
| CH3 | 46.6 | CH2 + H | 44.42 | -2.2(-4.7)\* |
| CH3 | 46.6 | CH + H2 | 44.37 | -2.2(-4.8) |
| CH3 | 46.6 | C + H2 + H | 42.7 | -3.9(-8.4) |
| CH3 | 46.6 | CH + 2H | 41.8 | -4.8(-10.3) |
| CH3 | 46.6 | C + H3 | 41.5 | -5.1(-10.9) |
| CH3 | 46.6 | CH2+ + H- | 38.1 | -8.5(-18.2) |
| CH3 | 46.6 | CH+ + H- + H | 35.6 | -11.0(-23.6) |
|  |  |  |  |  |
| CH3+ | 55.9 | CH2+ + H | 52.4 | -3.5(-6.3)\* |
| CH3+ | 55.9 | CH+ + H2 | 51.8 | -4.1(-7.3) |
| CH3+ | 55.9 | CH2 + H+ | 50.9 | -5.0(-8.9) |
| CH3+ | 55.9 | C + H3+ | 49.5 | -6.4(-11.4) |
| CH3+ | 55.9 | CH+ H2+ | 48.9 | -7.0(-12.5) |
| CH3+ | 55.9  | CH+ + 2H  | 48.5 | -7.4(-13.2) |
| CH3+ | 55.9 | C+ + H3 | 48.5 | -7.4(-13.2) |
| CH3+ | 55.9 | CH + H + H+ | 47.6 | -8.3(-14.8) |
| CH3+ | 55.9 | C+ +3 H | 46.8 | -9.1(-16.3) |
| CH3+ | 55.9 | C + 2H + H+ | 45.5 | -10.4(-18.6) |
|  |  |  |  |  |
| CH32+ | 60.5 | CH22+ + H | 59.8 | -0.7(-1.2)\* |
| CH32+ | 60.5 | CH+ + H2+ | 59.2 | -1.3(-2.1) |
| CH32+ | 60.5 | CH2+ + H+ | 62.7 | 2.2(3.6) |
| CH32+ | 60.5 | CH+ + H + H+ | 57.4 | -3.1-(5.1) |
| CH32+ | 60.5 | CH + 2H+ | 56.1 | -4.4-(7.3) |
| CH32+ | 60.5 | C + H + 2H+  | 53.3 | -7.2(-11.9) |
|  |  |  |  |  |
| CH4 | 43.5 | CH2 + H2 | 42.0 | -1.5(-3.4)\* |
| CH4 | 43.5 | CH3 + H | 41.6 | -1.9(-4.4) |
| CH4 | 43.5 | C + 2H2 | 40.5 | -3.0(-6.9) |
| CH4 | 43.5 | CH2 + 2H | 39.9 | -3.6(-8.3) |
| CH4 | 43.5 | CH + H3 | 38.9 | -4.6(-10.6) |
| CH4 | 43.5 | CH + 3H  | 37.8 | -5.7(-13.1) |
| CH4 | 43.5 | C + 4H  | 36.5 | -7.0(-16.1) |
| CH4 | 43.5 | C+ + H- + H3  | 32.6 | -10.9(-25.1) |
|  |  |  |  |  |
| CH4+ | 48.9 | CH2+ +H2 | 48.4 | -0.5(-1.0)\* |
| CH4+ | 48.9 | CH3+ + H | 48.3 | -0.6(-1.2) |
| CH4+ | 48.9 | CH3 + H+ | 46.6 | -2.3(-4.7) |
| CH4+ | 48.9 | CH2 + H2+ | 45.5 | -2.4(-4.9) |
| CH4+ | 48.9 | CH2+ + 2H | 45.6 | -3.3(-6.7) |
| CH4+ | 48.9 | CH + H3+ | 45.0 | -3.9(-8.0) |
| CH4+ | 48.9 | CH2 + H + H+ | 44.4 | -4.5(-9.2) |
| CH4+ | 48.9 | CH + H2 + H+ | 44.4 | -4.5(-9.2) |
| CH4+ | 48.9 | CH+ + H3 | 44.0 | -4.9(-10.0) |
| CH4+ | 48.9 | CH+ + 3H  | 42.6 | -6.3(-12.9) |
| CH4+ | 48.9 | CH +2 H + H+ | 41.8 | -7.1(-14.5) |
| CH4+ | 48.9 | C + H3 + H+ | 41.5 | -7.4(-15.1) |
|  |  |  |  |  |
| CH42+ | 54.1 | CH2+ + H2+ | 53.9 | -0.2(-0.4)\* |
| CH42+ | 54.1 | CH2+ + H + H+ | 52.4 | -1.7(-3.1) |
| CH42+ | 54.1 | CH3+ + H+ | 55.9 | 1.8(3.3) |
| CH42+ | 54.1 | CH+ + H2 + H+ | 51.8 | -2.3(-4.3) |
| CH42+ | 54.1 | CH32+ + H | 50.8 | -3.3(-6.1) |
| CH42+ | 54.1 | C+ + H2 + 2H+ | 48.6 | -5.5(-10.2) |
| CH42+ | 54.1 | CH+ + 2H + H+ | 48.5 | -5.6(-10.4) |
| CH42+ | 54.1 | CH + H + 2H+  | 47.6 | -6.5(-12.0) |
| CH42+ | 54.1 | C + 2H +2 H+  | 45.5 | -8.6(-15.9) |

a ΔI0 is defined as column 4 minus column 2.

b Calculated as ΔI0/I0 in %

c The asterisk indicates the composition for which we find the best agreement between the directly calculated mean excitation energy and the one obtained using Bragg’s rule.

Table 3. Comparison of molecular, RPA mean excitation energies (in eV) of nitrogen hydride molecules and molecular ions from Table 2 of [7] with those obtained using Bragg’s rule in Eq. (5) and I0i from [8,9] for the atomic fragments and from [7,10] for the molecular fragments.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Molecule/ion | I0 from [7] | fragments | I0 from Eq. (5) | ΔI0a(in %b)c |
| NH | 69.2 | N + H | 66.0 | -3.2(-4.6)\* |
| NH | 69.2 | N- + H+ | 57.5 | -11.7(-16.9) |
| NH | 69.2 | N+ + H- | 53.7 | -15.5(-22.4) |
|  |  |  |  |  |
| NH+ | 80.8d | N+ + H | 81.1 | 0.3(0.4)\* |
| NH+ | 80.8d | N + H+ | 81.6 | 0.8(1.0) |
| NH+ | 80.8d | N2+ + H- | 59.5 | -21.3(-26.4) |
|  |  |  |  |  |
| NH2 | 60.8 | N + H2 | 59.4 | -1.4(-2.3)\* |
| NH2 | 60.8 | NH + H | 58.4 | -2.4(-3.9) |
| NH2 | 60.8 | N + 2H | 56.0 | -4.8(-7.9) |
|  |  |  |  |  |
| NH2+ | 74.1 | N+ + H2 | 70.1 | -4.0(-5.4)\* |
| NH2+ | 74.1 | NH + H+ | 69.2 | -4.9(-6.6) |
| NH2+ | 74.1 | N + H2+ | 67.8 | -6.3(-8.5)\* |
| NH2+ | 74.1 | N+ + 2H | 65.7 | -8.4(-11.3) |
| NH2+ | 74.1 | NH+ + H | 65.5 | -8.6(-11.6) |
|  |  |  |  |  |
| NH22+ | 86.0 | N+ + H2+ | 83.6 | -2.4(-2.8)\* |
| NH22+ | 86.0 | N + 2H+ | 81.6 | -4.4(-5.1) |
| NH22+ | 86.0 | N++ H + H+ | 81.1 | -4.9(-5.7) |
| NH22+ | 86.0 | NH+ + H+ | 80.8 | -5.2(-6.0) |
| NH22+ | 86.0 | N2+ + H2 | 80.7 | -5.3(-6.2) |
|  |  |  |  |  |
| NH3 | 54.9 | NH + H2 | 53.7 | -1.2(-2.2)\* |
| NH3 | 54.9 | NH2 + H | 52.9 | -2.0(-3.6) |
| NH3 | 54.9 | N + H2 + H | 51.7 | -3.2(-5.8) |
| NH3 | 54.9 | NH + 2H | 51.0 | -3.9(-7.1) |
| NH3 | 54.9 | N + H3 | 50.5 | -4.4(-8.0) |
| NH3 | 54.9 | N + 3H | 49.1 | -5.8(-10.6) |
|  |  |  |  |  |
| NH3+ | 65.6 | NH2+ + H | 62.0 | -3.6(-5.5)\* |
| NH3+ | 65.6 | NH2 + H+ | 60.8 | -4.8(-7.3) |
| NH3+ | 65.6 | N + H3+ | 60.3 | -5.3(-8.1) |
| NH3+ | 65.6 | NH + H2+ | 59.8 | -5.8(-8.8) |
| NH3+ | 65.6 | N + H2 + H+ | 59.4 | -6.2( -9.5) |
| NH3+ | 65.6 | N+ + H2 + H | 59.1 | -6.5(-9.9) |
| NH3+ | 65.6 | N+ + H3 | 57.5 | -8.1(-12.3) |
| NH3+ | 65.6 | NH+ + H2 | 56.5 | -9.1(-13.9) |
|  |  |  |  |  |
| NH32+ | 74.2 | NH2+ + H+ | 74.1 | -0.1(-0.1)\* |
| NH32+ | 74.2 | N+ + H3+ | 71.3 | -2.9(-3.9) |
| NH32+ | 74.2 | NH + 2H+ | 69.2 | -5.0(-6.7) |
| NH32+ | 74.2 | NH22+ + H | 69.1 | -5.1(-6.9) |
| NH32+ | 74.2 | NH+ + H2+ | 67.2 | -7.0(-9.4) |

a ΔI0 is defined as column 4 minus column 2.

b Calculated as ΔI0/I0(ref. 2) in %

c The asterisk indicates the composition for which we find the best agreement between the directly calculated mean excitation energy and the one obtained using Bragg’s rule.

d During this work we discovered an error in the reported value for I0(NH+) in [7]. The corrected value is given in this table.

1. **Discussion**

The general picture that emerges from Tables 1-3 is that Bragg’s rule tends to underestimate the mean excitation energies, *i.e.* the binding effects ignored by Bragg’s rule for gas phase molecules give a positive contribution to the mean excitation energy. The few exceptions to this rule are provided by a couple charged ions and H3.

Furthermore, for all molecules but the smallest ones the ΔI0 values in Tables 1-3 that give the best fulfilment of Bragg’s rule rarely exceed 5 % and often they are even smaller than that. Changing I0 by ΔI0 gives a change in the logarithmic term in Eq. (3) of ΔI0/I0. Thus, with I0 of the order of magnitude in Tables 1-3 this implies that an error of the order 5 % in the mean excitation energy will give an error of the order 1 % in the Bethe stopping cross section. Hence, using the best fragmentation in the application of Bragg’s rule introduces very small errors in the molecular stopping power for the tested molecules and molecular ions.

On the other hand our results also indicate that the choice of fragmentation is important for the fulfilment of Bragg’s rule. The original application of Bragg’s rule consisted of subdividing a molecule into its constituent atoms. However, the fully atomic fragmentation does not give the best agreement between the correct I0 and I0 obtained using the Bragg rule for any but the obvious diatomic molecules or molecular ions. For instance, for NH3 an atomic fragmentation has an error of 6 % while the best fragmentation, NH + H2, carries an error of only 2 %. This difference is even larger for molecular ions.

Instead of using an atomic fragmentation, relying on chemistry is a good guideline for determining the fragmentation pattern that gives the best stopping cross section calculated from Eq. (1), an observation that has been used extensively [11-18] to obtain stopping cross sections and mean excitation energies for larger molecules.

The results in Tables 1-3 may also be used to draw a few additional conclusions about the fragmentation that gives the best fulfilment of Bragg’s rule for the molecules and molecular ions that we are considering here:

1. For neutral diatomic molecules, the best Bragg rule value for I0 is always obtained splitting the molecule up into its two neutral atomic constituents.
2. Splitting a compound up into more than two fragments is rarely a good idea.
3. For the neutral, polyatomic carbon and nitrogen hydrides, Bragg’s rule works best when the H2 molecule is one of the fragments, but very similar results are obtained when H is one of the fragments.
4. The optimal Bragg rule results for the positively charged carbon and nitrogen hydrides are obtained when the charge of the carbon/nitrogen fragment is larger than or equal to the charge of the hydrogen fragment.
5. We find that best dissociation fragments for XH, XH+, XH2, XH2+ , and XH3+ are the same for X = C and N.

As mentioned earlier Zeiss *et al.* [3] have tested the validity of Bragg’s rule for small molecules using an approach similar to ours. Even though they used a different approach for the determination of the mean excitation energies of molecules and atoms that we do, it would be interesting to see if their conclusions concerning the errors in mean excitation energies calculated using Bragg’s rule are like what we find here. To test that we have calculated the molecular mean excitation energies for the same molecules as they have done in their test and the results are given in Table 4.

Table 4. Comparison of predictions of molecular mean excitation energies (in eV) using Bragg’s rule.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Molecule | Molecular I0a | Bragg rule I0a,c | Molecular I0b | Bragg rule I0b,c |
| H2 | 19.3 | 15.0(-22%) | 19.5 | 15.0(-23 %) |
| N2 | 81.4 | 78.8(-3 %) | 83.5 | 81.6(-2 %) |
| O2 | 95.0 | 93.7(-1 %) | 96.8 | 97.9(1 %) |
| NH3 | 53.7 | 47.9(-11 %) | 54.9 | 49.1(-11 %) |
| H2O | 71.6 | 64.9(-9 %) | 73.0 | 67.3(-8 %) |
| N2O | 84.9 | 83.9(-1 %) | 86.7 | 87.2(1 %) |

a Zeiss *et al.* [3].

b This work.

c In parentheses we give the difference between the directly calculated molecular mean excitation energy and the one obtained using Bragg’s rule (in per cent).

Even though the individual mean excitation energies are a bit different due to the difference in methods used to generate them, we see the conclusions with respect to the fulfilment of Bragg’s rule are nearly identical. Thus, one may conclude that for the examples tested here the fulfilment of Bragg’s rule is not dependent on the method used to obtain the mean excitation energies but is a coupled to the nature of the chemical binding in the molecules.

It appears that the hydrides are the ones which show the largest effect of binding whereas the binding effects are less pronounced when the individual atoms have a ‘sufficiently’ large number of electrons. This conclusion is understandable as we know that it is excitation out of the core that gives the largest contributions to the mean excitation energy and the excitations out of the core make up a larger fraction of I0 in the non-hydrides than in the hydrides.

1. **Summary**

For a series of small molecules and their ions we have investigated the effect of chemical binding on mean excitation energies that are ignored when applying Bragg’s rule to the calculation of stopping cross sections.

The sign of the error on I0 due to neglect of chemical binding is nearly always negative, that is, when using Bragg’s rule smaller mean excitation energies and consequently larger stopping cross sections are obtained. However, if we use the optimal fragmentation of the molecule, guided by chemical intuition, this error may be rather small. In the cases tested here the error in the stopping cross section does not exceed 1 % when the best decomposition is applied.

For all but diatomic molecules and molecular ions a fully atomic decomposition of the molecule does not represent the optimal fragmentation. Every time a bond is broken a contribution to the mean excitation energy is missing, so it quite understandable that a fragmentation with as few fragments as possible will give the best fulfilment of Bragg’s rule. This trend is clearly illustrated in the fragmentation patterns displayed in Tables 1-3.

Thus, the very simple, and rather obvious, conclusion you may draw from our test cases is that you must break as few bonds as possible if you wish to reduce the binding effect on the validity of the Bragg rule.

For each molecule we are studying several fragmentation possibilities. The common trends in these fragmentation patterns allow us to draw conclusions about the choices of fragmentation that gives the best fulfillments of the Bragg rule prediction of mean excitation energy.

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