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Balmer-α emission cross sections from collisions of He^+ on H_2, CH_4, C_2H_2, C_2H_4, and C_2H_6: A study of Bragg additivity

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Bragg additivity was explored through measurement of Balmer-α emission cross sections produced by the collision of 100–350-keV He^+ incident on H_2, CH_4, C_2H_2 C_2H_4, and C_2H_6. The cross-section data show a linear relation on a Fano plot, thus indicating that the Bethe-Born theory may provide an appropriate description of the collision. Evidence for Bragg additivity would be a direct dependence of the value of the emission cross section on the number of hydrogen atoms in the target molecule. Results indicate a failure of strict additivity. Once molecular structure had been taken into account by a calculation of approximate electron densities, the cross sections followed an additive rule demonstrating a dependency not only on the number of hydrogens present, but also on the number of electrons available per hydrogen atom.

INTRODUCTION

Ion-molecule collisions have been studied extensively with relatively simple targets such as H_2 and N_2. There is little data, however, for more complex molecular species. We report here cross sections for Balmer-α emission resulting from collisions of 100–350-keV He^+ on various hydrocarbons. Such cross sections can be useful in fusion research.[1] Because of recent studies of the validity of the additive rule, we also look at the results of our cross-section data with regard to additivity.

The photon emission produced in the study came from the following general process:

$$He^+ + C_nH_m \rightarrow (C_nH_m)^* \rightarrow C_nH_{m-1} + H^* . \qquad (1)$$

If, as according to the Bragg rule, the hydrocarbon molecules act as a collection of atoms, the Balmer photon-emission cross section would be directly dependent only on the number of hydrogen atoms present in the target molecule. Our results suggest a more sophisticated relationship.

There appears to be no previous studies of He^+ on hydrocarbons producing Balmer-α emission in this energy range. Several studies, however, have been done with other beams. Geddes, Yousif, and Gilbody have reported on Balmer-α cross sections for H, H^+, H_2^+, and H_3^+ on CH_4.[2] Carré and Dufay found Balmer emission cross sections for 30–600-keV protons on CH_4, C_2H_2, C_2H_4, and C_2H_6.[3] Williams *et al.* studied Balmer-α emission in collisions of H, H^+, H_2^+, and H_3^+ with H_2.[4]

Although the authors could find no studies of the additivity rule in photon-emission cross sections, other studies have investigated the additivity rule in charge-transfer processes, often with the motivation of finding atomic cross sections from molecular targets. Wittkower and Betz[5] reported a failure of the additivity rule in charge changing cross sections for heavy 12-MeV ions on complex target molecules. Toburen *et al.*[6] and Sataka *et al.*[7] estimated atomic carbon charge-transfer cross sections from cross sections of various carbon-containing molecules using, respectively, H^+ and H at 100–2500 keV and He^+ and He at 300–1800 keV. Neither, however, attempted to take into account molecular structure in their calculations. Itoh *et al.*[8] also estimated the electron transfer cross sections for He^+ beams incident on atomic carbon and showed that, at a higher-energy range than investigated here (700–2000 keV), the additivity rule applied. Their values, however, were 4–12 times smaller than those of Sataka.

At similar energies Varghese *et al.*,[9] reporting on atomic total electron-capture cross sections from H^+ and He^+ projectiles, showed additivity failure in various C_mX_n molecular species. They discussed two possible explanations for additivity failure, originally presented by Bissinger *et al.*,[10] both of which take into account molecular effects. One explanation involved intramolecular electron-loss processes which, when corrected for, allowed the extraction of atomic cross sections. At the energies of their work, a second molecular effect, the alterations of electron distributions and binding energies, resulted in only 2% variation in cross sections and thus, they concluded, have negligible effect.[9] At lower energies, however, they suggested that these molecular alterations may have a larger effect and may be the cause of additivity failure. In addition to investigating the validity of the Bragg additivity rule, this paper presents a first step in correcting Bragg additivity for molecular structure in the case of Balmer-α emission in the energy range of 100–350 keV.

EXPERIMENTAL PROCEDURE

Details of the experimental apparatus have been described previously.[11,12] Briefly, a beam of helium ions was produced by a Van de Graaff accelerator and momentum analyzed by a 90° magnet. The beam entered a differentially pumped target chamber after being collimated to approximately 2–3 mm. After passing through a target gas cell, the beam was collected by a

Faraday cup. Photons emitted at 90° to the beam direction were analyzed by a monochrometer set at 6563 Å and detected by a photomultiplier tube. The resolution of the monochrometer was greater than the linewidth so all emitted photons from that line were counted. The photon detection system was calibrated with respect to its absolute sensitivity by standard techniques, and corrections were made for polarization and anisotropy effects[13] through the use of a polarizing filter whose axis of polarization could be set parallel or perpendicular to the beam line.

Relative photon yields as a function of target gas pressure were found to be linear up to a pressure of 5 mTorr. Single-collision conditions were maintained by using a target-gas pressure of 3 mTorr which was measured by a capacitance manometer. Temperature was measured by a thermistor. Typical ion beam currents were on the order of 0.3 μA.

A major correction to the data involved accounting for beam neutralization in the beam current measurement. The attenuation in the beam was calculated by measuring the beam current on both the Faraday cup and collimator with no gas in the target chamber. Target gas was then introduced and a second measurement was taken to produce a neutralization ratio. Figure 1 shows the beam attenuation for each hydrocarbon as a function of energy.

Figure 2 shows a block diagram of the electronic system used in data acquisition which differs from that used in previous work from this laboratory. Signals from the capacitance manometer, the monochromator, the thermistor, the Faraday cup, and the photomultiplier tube (PMT) [via a single-channel analyzer (SCA)] were fed into the Keithley 500A data acquisition system, which performed analog-to-digital conversion of these voltage signals and channeled them to the IBM PS/2 80 computer. This data was then assimilated by programs written in ASYST3.0 to produce cross sections corrected for beam current, temperature, gas pressure, and optical system sensitivity. A signal from the computer rotated the polarizing filter by 90° during cross-section measurements. To find the correction for beam attenuation, the beam current from the collimator and Faraday cup was converted into a voltage signal and read by the computer through the Keithley for both 0 and 3 mTorr.

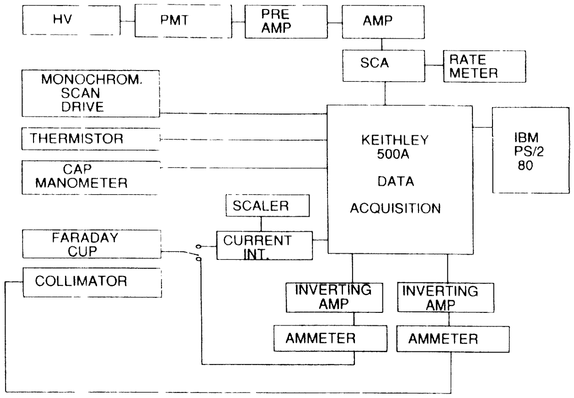

FIG. 2. Block diagram of the electronics used.

The estimated error due to experimental systematics in all the absolute photon emission cross sections reported here is 20%. Approximately three-quarters of the error is due to measurement of the sensitivity of the optical systems, while one-quarter is due to statistical uncertainty and error from measurements of the target pressure, temperature, and beam current.

RESULTS AND DISCUSSION

Figure 3 shows the results for the Balmer-α emission cross sections of 100–350-keV He^+ beam on H_2, CH_4, C_2H_2, C_2H_4, and C_2H_6. The values are listed in Table I.

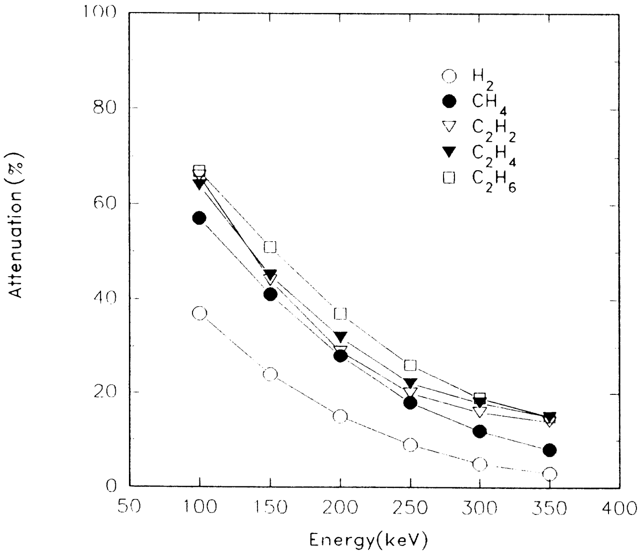

FIG. 1. Percent attenuation of the He^+ beam as a function of beam energy. Uncertainty of the data is 9%.

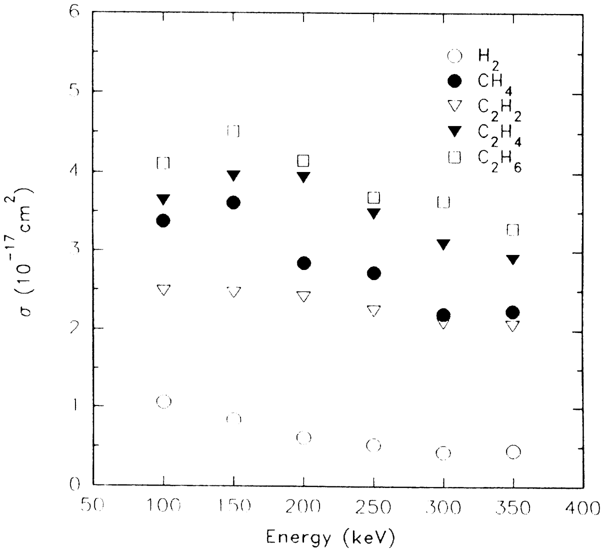

FIG. 3. Balmer-α cross sections for investigated target molecules as a function of energy. The error in the data is 20% for all cross sections.

TABLE I. Balmer-α photon-emission cross sections. Units are 10^{-17} cm^2, uncertainty is 20%.

Energy (keV)	H_2	C_2H_2	CH_4	C_2H_4	C_2H_6
100	1.06	2.48	3.37	3.64	4.11
150	0.843	2.46	3.61	3.95	4.51
200	0.616	2.41	2.84	3.94	4.15
250	0.523	2.24	2.72	3.48	3.69
300	0.438	2.09	2.20	3.09	3.64
350	0.455	2.06	2.24	2.90	3.29

Since the authors could find no previous data of helium ions on hydrocarbons producing Balmer-α emission, we used as the basis of comparison, reported cross sections for protons of comparable velocities on H_2 and various hydrocarbons.[1-3] Our cross sections fall within a factor of 2 to Williams' cross sections of H^+ on H_2 at the same velocities. For CH_4 our values deviate from both Carré and Geddes by about a factor of 3. These differences are most likely accounted for by the differences in the calibration of the optical systems. The location of the maxima of the photon-emission cross sections in this work at around 35 keV/u is comparable to the location of the maxima found at similar velocities by other studies.[1,3] Geddes *et al.* found a maximum for the CH_4 target at about 25 keV/u which is comparable to our velocity maximum for CH_4 at about 37.5 keV/u. Williams *et al.* found a maximum for a hydrogen target at about 20 keV/u, a velocity lower than those investigated here.

Previous work from this lab has shown that the Bethe-Born theory may be applicable in the case of photon emission from target excitation.[14] An indication that the Bethe-Born theory may be applicable is a linear fit on a Fano plot.[15] Figure 4 is a Fano plot for the cross sections of the target molecules. The line fit for all targets, using a least-squares approximation, is quite good. Thus, the Bethe-Born theory may be an appropriate description of the collision process.

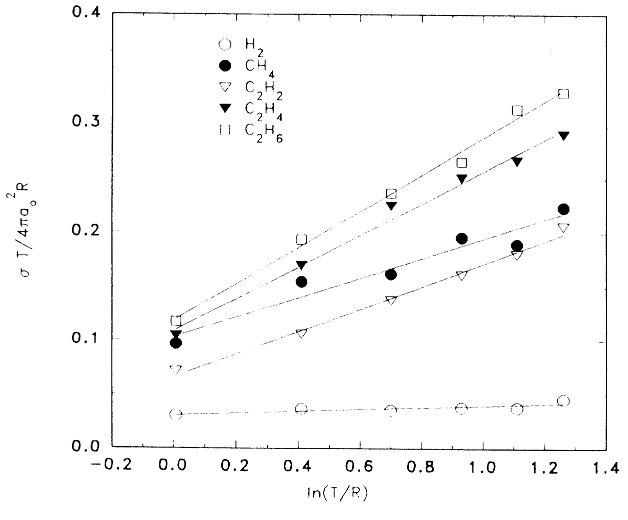

FIG. 4. Fano plots for the Balmer-α emission cross sections of various target molecules. T/R is the kinetic energy of the projectile divided by the Rydberg energy; a_0 is the Bohr radius.

Bragg additivity states that a molecule acts as a collection of its constituent atoms. This implies that the Balmer-α emission cross section should be dependent only on the number of hydrogen atoms present. If this were the case, the following relationship would hold:

$$\frac{2}{n}\sigma(C_mH_n)=\sigma(H_2)\ , \tag{2}$$

where n is the number of hydrogen atoms in the hydrocarbon. For example,

$$\tfrac{1}{3}\sigma(C_2H_6)=\sigma(H_2)\ . \tag{3}$$

Figure 5 shows the cross sections corrected for Bragg additivity, σ_c:

$$\sigma_c(C_mH_n)=\frac{2}{n}\sigma(C_mH_n)\ . \tag{4}$$

Each cross section $\sigma(C_mH_n)$ was divided by $n/2$ and, if Bragg additivity holds true, then these values should fall on the cross section for H_2. This is obviously not the case; something more must be taken into account.

The process producing a Balmer-α emission should depend not only on the number of hydrogen atoms present, but also on the number of electrons available to the dissociating proton. This, in turn, will be dependent on the molecular structure of the hydrocarbon. If Bragg additivity held for Balmer-α emission cross sections, the electron density surrounding a proton in a hydrocarbon would be the same as that of a lone hydrogen atom. The molecular structure, however, produces different electron densities which must be deduced from molecular orbital calculations.

Here we present a simple method for approximating the number of electrons available to each hydrogen by using the results of molecular SCF calculations.[16,17] We assume that the number of electrons available to any one hydrogen in a hydrocarbon containing n hydrogens will be $(1/n)(N_{\text{tot}}-N_{\text{C—C}})$, where N_{tot} is the total number of electrons and $N_{\text{C—C}}$ is the number of electrons involved only in C—C bonding. H_2 and CH_4 will obviously have no electrons involved in C—C bonding. Thus, as can be seen in Table II, the number of electrons available to each hydrogen in these molecules will simply be the total number of electrons divided by the number of hydrogens. In C_2H_2 and C_2H_4 there are triple and double C—C bonds, respectively, which involve molecular orbitals with π character contributing very little to C—H bonds. Table

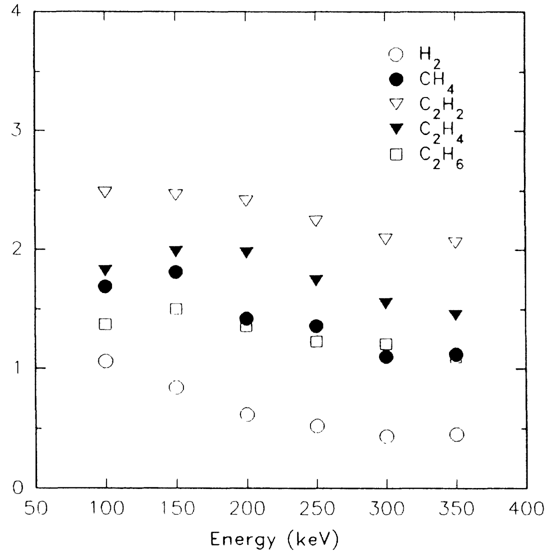

FIG. 5. Cross sections corrected for Bragg additivity (σ_c). The cross sections of each hydrocarbon have been divided by $\frac{1}{2}$ the number of hydrogen atoms contained in the molecule.

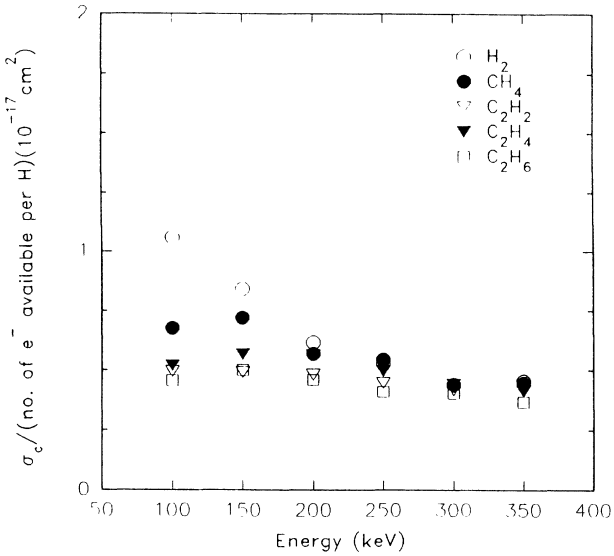

FIG. 6. Cross sections with corrections for electron densities. Cross sections (σ_c) were divided by the number of electrons available to each dissociating hydrogen.

II lists these orbitals and the number of electrons in each. C_2H_6, having only a single carbon bond, contains no π bonds solely involved in C—C bonding, and therefore no electrons were subtracted from the total number in finding the number of electrons available to a hydrogen. A similar method of approximation has been presented previously by Bissinger, Joyce, Tanis, and Varghese.[18] They observed 2-MeV-proton-induced carbon K x-ray yields from a series of carbon-bearing molecules. Their statistical model suggests that the number of p-character valence electrons available to fill a K vacancy is proportional to the x-ray yields.

Figure 6 shows the Bragg corrected cross sections (σ_c) divided by the number of electrons available per hydrogen atom. At the higher energies, Bragg additivity, with the correction for electron densities, seems to be a very good model. The discrepancies at the lower energies can be accounted for by examining the difference in the behavior of the cross sections of each molecule. At the lower energies, the photon-emission cross sections reach maxima at different projectile velocities for different target molecules. Therefore, the differences in behavior due to projectile velocity dependence causes deviations from an additive rule which cannot be accounted for by electron density corrections. It is only at the higher energies where all the cross sections are behaving in a $(1/v^2)\ln v$ fashion that these corrections can be applied.

Although this correction for the electron population is admittedly simple, it does seem to recover the additivity rule and is consistent with the technique employed by Bissinger *et al.*[15]

CONCLUSION

We have measured the Balmer-α emission cross section for hydrogen atoms and various hydrocarbons from a 100–350-keV helium ion beam and found them relatively consistent with those measured for a hydrogen beam at similar velocities. Also, a Fano plot indicated that the

TABLE II. Derivation of electrons involved in hydrogen bonding. NA denotes "not applicable."

Molecule	Total electrons	Orbitals involved only in C—C bonding	Number of electrons involved only in C—C bonding	Number of electrons involved in C—H bonding per H
H_2	2	NA	0	1
CH_4	10	NA	0	2.5
C_2H_2	14	$1\pi_{ux}$, $1\pi_{uy}$	4	5
C_2H_4	16	$1b_{2u}$	2	3.5
C_2H_6	18		0	3

Bethe-Born theory could be used to describe the collision. Our results showed a failure of straight Bragg additivity at these energies. We suggest a method of correction which accounts for molecular structure by approximating electron densities. The correction we have applied to the data is a first step in this process and has produced surprisingly good results.

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