Table I were obtained. The absolute cross section for production of atoms in the $3S$ state was determined from the target pressure, the detection efficiencies, and the $3S$ population parameter found in the least-squares fits. Table I also summarizes the results from other experiments.[9,10]

The measurements show that electron capture into the $3S$ state dominates and that the cross sections decrease with increasing L. The cross sections for capture into the different M_L states decrease with increasing $|M_L|$. The partial cross sections for production of atoms in the P and D states agree satisfactorily with the measurements of Hughes *et al.*[9] and the extrapolated measurements of Ford and Thomas.[10] There are no theoretical predictions for the partial cross sections for electron capture from a nitrogen target. The reported calculations for electron capture from an atomic hydrogen target vary by more than a factor of 2 from one calculation to another.

In summary this paper reports the first complete determinations of the partial cross sections for capture into each of the L, M_L states for the $n=3$ manifold. With some modifications in the design of the apparatus the precision of the measurements can be improved. In particular the measurement of the absolute cross section can be increased by an order of magnitude. We plan to use this method with an atomic hydrogen target to measure the cross sections for protons incident on hydrogen atoms and thus make an unambiguous test of the theoretical calculations.

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[1] B. H. Bransden, in *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and B. Bederson (Academic, New York, 1975), Vol. 15, p. 263.

[2] Dz. Belkic *et al.*, Phys. Rep. 56, 279 (1979).

[3] D. Basu *et al.*, Phys. Rep. 42, 145 (1978).

[4] J. Delos, Rev. Mod. Phys. 53, 287 (1981).

[5] F. M. Piplin, in *Atomic Physics 4*, edited by G. zu Putlitz, E. W. Weber, and A. Winnacker (Plenum, New York, 1975), p. 119.

[6] M. P. Silverman and F. M. Pipkin, J. Phys. B 7, 704 (1974).

[7] M. P. Silverman and F. M. Pipkin, J. Phys. B 7, 730 (1974).

[8] M. P. Silverman and F. M. Pipkin, J. Phys. B 7, 747 (1974).

[9] R. H. Hughes *et al.*, Phys. Rev. A 1, 1424 (1970).

[10] J. C. Ford and E. W. Thomas, Phys. Rev. A 5, 1701 (1972). These measurements covered the range of 80–400 keV and were extrapolated to 49 keV to obtain the cross sections quoted in Table I.

Failure of Cross-Section Additivity for Electron Capture from Hydrocarbon Gases to Bound States of Hydrogen Ions

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The measured total electron-capture cross sections per number of carbon atoms in C_mH_n ($m=1,2,3,4$), σ_c/m, decrease with increasing m. This decrease is largest at the lowest velocities of 0.8–3 MeV ${}^1_1H^+$ ions, and diminishes in the limit of high velocities where the strict additivity of atomic cross sections in a molecular target is approached. The breakdown of the additivity rule in the present data is primarily attributed to, and accounted for in terms of, intramolecular electron loss processes.

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According to the additivity rule the value of a quantity of interest for a molecular target is equal to the sum of the values of these quantities for the constituent atoms in the molecule. The uncontested utility of this rule is marred by questions as to the range of its validity. As an example, the stopping power of a compound is often determined as the sum of stopping powers for its elements (Bragg rule).[1] The validity of this additivity rule outside the high-velocity limit becomes, however, questionable.[2] Significant deviations from the additivity rule were seen in other phenomena such as photoionization,[3] Auger-electron and x-ray production in inner-shell ionization,[4] or pion capture from complex materials.[5] Such deviations were also noticed in electron-capture processes[6] and prompted Betz to remark that "...no simple rule can accurately describe the cross sections for complex molecules on the basis of the cross sections for the single atoms."[7] He adds further that "a convincing explanation (of the additivity failure) has not yet been given."

In recent communications,[8] we have reported the data that reflect the breakdown of the additivity rule for electron-capture cross sections. In this work, we systematically examine additivity failure for electron capture by megaelectronvolt protons as a function of the composition of gaseous hydrocarbon (C_mH_n; $m = 1-4$) target molecules and the speed (5.7–11 a.u.) of the projectile. We offer here a quantitative explanation of the observed trends in the breakdown of the additivity rule in terms of *intramolecular* electron loss processes.

The experimental apparatus consisted of a standard differentially pumped gas cell with a 4×10^{-4}-cm^2 entrance aperture and 2×10^{-2}-cm^2 exit aperture followed by an antiscattering aperture. The H^+ beam was provided by the 2-MV tandem Van de Graff accelerator at East Carolina University. After the ion beam traversed the gas cell the protons were magnetically deflected into a Faraday cup, while the neutral hydrogen beam fraction went straight into a surface barrier detector. Beam currents were limited to 10–100 pA so that count rates would not lead to system dead times greater than 15%–20%. Current integrations at the lower currents required current amplification by an intermediate electrometer. The typical feedback-regulated (± 1%) gas pressure in the gas cell was 10 mTorr and was monitored via a 0–1 Torr capacitance manometer. In all cases, data were accumulated at pressures in the linear portion of the target-gas-pressure versus neutrals-count curve. The charge transfer outside the gas cell proper, ranging from 6%–11% of the total, was corrected for by the expedient of leaking gas directly into the target chamber to attain the same beam-line ionization gauge reading. The small end corrections, Δl, to the gas cell length, $l = 1.9$ cm, cancel in the relative cross sections and did not exceed 7%. The measured neutral beam yield, Y^0, and the collected charge, Y^+, give the charge transfer cross section $\sigma_c = Y^0/N(l+\Delta l)Y^+$ (where N is the number of molecules per cubic centimeter).

The electron-capture cross sections for each hydrocarbon $\sigma_c{}^{C_mH_n}$, are simply

$$\sigma_c{}^{C_mH_n} = m\sigma_c{}^{C} + n\sigma_c{}^{H} \tag{1}$$

if additivity holds. At the velocities of our experiment,[9] $\sigma_c{}^{H}$ is less than 1.6% of $\sigma_c{}^{C}$ so that the capture from hydrogen atoms can be neglected in Eq. (1). The ratios $\sigma_c{}^{C_mH_x}/\sigma_c{}^{C_mH_y}$ for $x \neq y$ are, within experimental uncertainties, indeed equal to unity at all projectile velocities in our experiments. For example, $\sigma_c{}^{C_2H_6}/\sigma_c{}^{C_2H_2} = 1.02 \pm 0.02$ for 0.8-MeV H^+. Thus

$$\sigma_c{}^{C_mH_n} \simeq \sigma_c{}^{C_m} \tag{2}$$

with $\sigma_c{}^{CH_4} \simeq \sigma_c{}^{C}$ for methane.

Let us define the ratio

$$R_c \equiv \sigma_c{}^{C_mH_n}/m\sigma_c{}^{CH_4}, \tag{3}$$

so that by Eq. (2) $R_c = 1$ when additivity holds. Our experimental values for R_c are listed in Table I. The systematic trends in R_c emerge: (i) $R_c \leq 1$; (ii) R_c decreases with increasing m (number of carbon atoms in the molecule) at constant projectile velocity; and (iii) R_c decreases with decreasing velocity at constant m. While departures from strict additivity have been noticed previously,[6] the small relative errors of this experiment allow us to observe systematic deviations from additivity, as m and projectile velocity are varied, with a considerable improvement in precision.

To trace the root causes of the additivity failure in molecular electron-capture cross sections, we separate the effects of molecular environment into what one might call "entrance" and "exit" effects. The former effect results from alterations of electron distributions (morphological

TABLE I. Experimental electron-capture cross sections per C atom for H^+ on various hydrocarbon gases relative to methane [R_c of Eq. (3); uncertainties in R_c are ± 2%].

	Projectile energy (MeV)			
Target gas	0.8	1.5	2.0	3.0
C_1H_4	1.00	1.00	1.00	1.00
C_2H_2 [a]	0.90	0.94	0.98	0.97
C_3H_6 [a]	0.84	0.92	0.93	0.94
C_4H_8 [a]	0.77	0.88	0.91	0.93

[a] All C_mH_n agreed within the uncertainties in R_c with each other for a given m and various n. The values listed here for specific n are typical.

change) and electron binding energies (chemical shifts) before the ion enters a "molecular" atom. The latter effect comes from *intra*molecular electron loss processes as the projectile-electron pair exits the molecule.

The ratio of electron-capture cross sections computed with molecular eigenfunctions and binding energies to those evaluated with atomic wave functions and energies is a measure of the entrance effect. *Ab initio* calculations of this type are at present a nearly impossible computational task. The magnitude of the entrance effect can be, nevertheless, estimated from the number of electrons of a given atomic origin in molecular orbitals[10] and from the observed binding energies of these electrons in molecules.[11] For example, for carbon, one can compare the atomic (2,2,2) population in the ($1s,2s,2p$) configuration with the molecular distributions (2.0, 1.4, 3.3) and (2.0, 1.2, 3.1) found in CH_4 and C_3H_6, respectively. Corresponding electron-capture cross sections per carbon atom for 0.8-MeV H^+ on these hydrocarbons are calculated according to Lapicki and co-workers[12] as 3.60, 3.66, and 3.61 ($\times 10^{-20}$ cm^2). Thus, the redistribution of the electrons leads to differences of less than 2%. Chemical shifts among any of these molecules result in at most 0.2% variations in the cross sections.[12] On the basis of these estimates the entrance effect is clearly not capable of the reduction in R_c that we observe. The inconsequential role of this effect is not surprising since at our relatively high velocities the dominant contribution to the total electron-capture cross section comes from the C K shell which remains relatively unaffected by the chemical milieu of the carbon atom.

An estimate of the exit effect is made in the following model calculation. A neutral fraction, f^0, for the beam of hydrogen atoms produced after electron capture from one of the atoms in a molecule, disintegrates as the hydrogen atoms exit the very same molecule. The projectile that captures an electron, on the average midway within the molecule, will lose and capture electrons to and from one half of the remaining atoms of the molecule. With x being the areal density of these atoms for the residual half-molecule, and with σ_c and σ_l standing for the capture and loss cross sections per atom, f^0 decreases from 1 at the center of the molecule to

$$f^0=\{\sigma_c+\sigma_l \exp[-(\sigma_c+\sigma_l)x]\}/(\sigma_c+\sigma_l), \qquad (4)$$

which is the solution of the standard rate equation[7] $df^0/dx=\sigma_c f^+ - \sigma_l f^0$ with $f^0+f^+=1$. The exponential extinction of f^0 in Eq. (4) is predominantly due to loss processes because $\sigma_c^{\mathrm{C,H}}/\sigma_l^{\mathrm{C,H}} \leq 10^{-3}$ for ~1-MeV protons.[9] Even for $\sigma_l x$ as large as 2.6 (considerably larger than in any of our cases), Eq. (4) can be approximated by

$$f^0 \simeq \exp(-\sigma_l x) \qquad (5)$$

to within 1%.

Since $\sigma_c^{\mathrm{H}}/\sigma_c^{\mathrm{C}} \leq 0.02$,[9] the captured electron comes essentially from a C atom; hence the loss occurs when the projectile traverses the remaining, on the average, $(m-1)/2$ carbon atoms and $n/2$ hydrogen atoms in a C_mH_n hydrocarbon. Therefore, $\sigma_l x$ in Eq. (5) is evaluated as

$$\sigma_l x=\tfrac{1}{2}(m-1)\sigma_l^{\mathrm{C}}x_{\mathrm{C}}+\tfrac{1}{2}n\sigma_l^{\mathrm{H}}x_{\mathrm{H}}, \qquad (6)$$

where $x_{\mathrm{C,H}}$ is the areal density of these atoms. Equation (6) obtains with a simplifying assumption that the molecule is linear; the beam then indeed traverses, on the average, one half of the molecular length. In a more rigorous approach that accounts for three-dimensional structure of molecules, some kind of spatial orientation averaging would have to be devised to determine the exit areal density in which electron loss occurs. Our estimates show that various averaging schemes, within the uncertainties in determination of $x_{\mathrm{C,H}}$, lead to nearly the same values as Eq. (6). We find $x_{\mathrm{C}}=d_{\mathrm{C}}\rho N_{\mathrm{A}}=2.1\times10^{15}$ cm^{-2}, where d_{C} is the average C-C spacing in the molecule, 1.3 Å, ρ is the density of solid C (diamond), 3.3 g cm^{-3}, and $N_{\mathrm{A}}=6.023\times10^{23}$ atoms/(12 g). Since each C comes with a pair of hydrogens, $x_{\mathrm{H}}=2x_{\mathrm{C}}$. In CH_4, however, we take $x_{\mathrm{H}}'=x_{\mathrm{H}}(1.1/1.3)$ to correct for the 1.1-Å C-H spacing in methane. Even for the largest values of σ_l^{C} and σ_l^{H} attained with 0.8-MeV protons (7×10^{-17} and 1.1×10^{-17} cm^2)[9] and the largest of the investigated hydrocarbons, C_4H_8, $\sigma_l x=0.29$ so that Eq. (4) is approximated by $\exp(-\sigma_l x)$ to better than 0.1%.

The neutral fraction, f^0, of projectiles created in the aftermath of capture is, as a result of the exit effect, diminished exponentially with increasing molecular size as well as with increasing loss cross sections, such as occurs for our experiment with decreasing projectile energy. The experimental neutral fractions exhibit both expected parameteric dependences. To compare with experiment, we calculate the theoretical value R_c^{theor} as

$$R_c^{\text{theor}} = \frac{f^0(C_mH_n)}{f^0(CH_4)} \simeq \exp[-(\sigma_l x)_{C_mH_n} + (\sigma_l x)_{CH_4}] = \exp\{-\tfrac{1}{2}[(m-1)\sigma_l{}^{C}x_{C} + n\sigma_l{}^{H}x_{H} - 4\sigma_l{}^{H}x_{H}']\}, \qquad (7)$$

with loss cross sections taken from Ref. 9.

The agreement between R_c of Eq. (3) and R_c^{theor} of Eq. (7), as shown in Fig. 1, is excellent. We observe here that when the cross sections for electron capture from molecules are divided by R_c^{theor}, i.e., when one is accounting for the exit effect, then the additivity rule is obeyed. The utility of this rule, for reliable extraction of electron-capture cross sections on atomic targets, is salvaged once such a correction to molecular data is made. Alternatively, the sum of the electron-capture cross sections calculated for atomic constituents of a molecule ought to be multiplied by R_c^{theor} of Eq. (7) for an accurate prediction of the electron-capture cross section from this molecule.

Contrary to our findings for protons, Itoh, Asari, and Fukuzawa[13] claim that the additivity rule is verified in their measurements of electron-capture cross sections from hydrocarbons by 0.7–2 MeV helium ions. Their assertion is made, however, with data that have considerably larger relative uncertainties than ours; their experimental error bars exceed in magnitude the expected deviations from the additivity rule. In fact, the trends in the data shown in Fig. 3 of Ref. 13 do indeed, on close scrutiny, point to the breakdown of the additivity rule with increasing m ($m = 1-3$) and decreasing projectile velocity. These trends agree with our observations[14] for 3.2-MeV He$^+$ on hydrocarbons where we found $R_c = 0.90 \pm 0.02$ ($m = 2$) and $R_c = 0.86 \pm 0.02$ ($m = 3$). We note also that these values of R_c as well as $R_c = 0.79 \pm 0.02$ ($m = 4$) coincide with the 0.8-MeV H$^+$ data (Table I), i.e., the additivity rule fails to the same extent for these different projectiles at identical velocities.

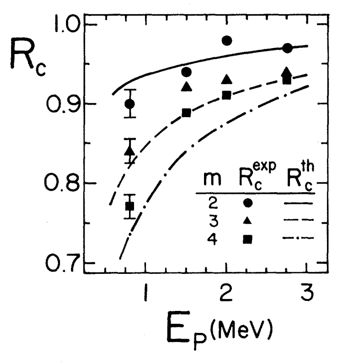

FIG. 1. Cross-section ratios, R_c, with respect to CH_4 and per carbon atom, for electron capture from C_mH_n ($m = 2-4$) by 0.8–3.0 MeV protons. Experimental points are from Table I; for clarity typical uncertainties are shown only at the lowest energy. Curves are calculated according to Eq. (7), which accounts for intramolecular loss processes.

At high velocities electron-loss cross sections decrease so that the mean free path for the survival of the projectile–captured-electron pair becomes orders of magnitude larger than the size of the molecule. Hence the additivity rule for total electron-capture cross sections is not broken at such velocities. A similar argument could be advanced at velocities sufficiently below the maximum in the electron-loss cross sections. The additivity rule could still, however, be violated on account of the entrance effect; the outer shells, which contribute predominantly to the total electron-capture cross sections at these low velocities, are most affected by changes in the molecular environment. At 5.7–11 a.u. speeds, the protons in our experiments are sufficiently fast to capture an electron mostly from the carbon K shell and yet they are sufficiently slow to detect significant deviations from the additivity rule.

In conclusion, we have observed additivity failure in electron capture to H$^+$ projectiles from molecular hydrocarbon gases.[15] At our velocities the additivity failure cannot be explained in terms of changes in electron-capture cross sections of atoms when they form a compound (entrance effect), but rather appears to arise predominantly from intramolecular electron-loss processes as the neutral H projectile exits the molecule (exit effect).

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[1] W. H. Bragg and R. Kleeman, Philos. Mag. 10, S318

(1905).

[2] J. W. Wilson, C. K. Chang, Y. J. Xu, and E. Kamaratos, J. Appl. Phys. **53**, 828 (1982), and references therein. Also, see W. Brandt, in Workshop on Current Stopping Power Problems, New York, January 1978, Summary Report, edited by G. Lapicki and S. Stern (unpublished), p. 244.

[3] R. D. Deslattes, Acta. Crystallogr., Sect. A **25**, 89 (1969); D. F. Jackson, Nucl. Instrum. Methods **193**, 387 (1982).

[4] R. P. Chaturvedi, D. J. Lynch, L. H. Toburen, and W. E. Wilson, Phys. Lett. **61A**, 101 (1977); K. G. Harrison, H. Tawara, and F. J. de Heer, Chem. Phys. Lett. **14**, 285 (1972); G. Bissinger, J. M. Joyce, J. A. Tanis, and S. L. Varghese, Phys. Rev. Lett. **44**, 241 (1980).

[5] D. F. Jackson, C. A. Lewis, K. O'Leary, and G. K. Y. Lam, Nature **295**, 557 (1982).

[6] A. B. Wittkower and H. D. Betz, J. Phys. B **4**, 1173 (1971).

[7] H. D. Betz, Rev. Mod. Phys. **44**, 465 (1972).

[8] S. L. Varghese, R. Laubert, J. M. Joyce, and G. Bissinger, IEEE Trans. Nucl. Sci. **28**, 1056 (1981).

[9] L. H. Toburen, M. Y. Nakai, and R. A. Langley, Phys. Rev. **171**, 114 (1968); R. Dagnac, D. Blanc, and D. Molina, J. Phys. B **3**, 1239 (1970).

[10] L. C. Snyder and H. Basch, *Molecular Wave Functions and Properties* (Wiley, New York, 1972). These numbers are deduced from the so-called Mulliken charges as tabulated from self-consistent-field calculations in a Gaussian basis set.

[11] T. A. Carlson, *Photoelectron and Auger Spectroscopy* (Plenum, New York, 1975); *Handbook of Chemistry and Physics*, edited by R. Weast (CRC Press, Cleveland, 1978–1979), 59th ed., p. E74.

[12] G. Lapicki and W. Losonsky, Phys. Rev. A **15**, 896 (1977); G. Lapicki and F. D. McDaniel, Phys. Rev. A **22**, 1896 (1980).

[13] A. Itoh, M. Asari, and F. Fukuzawa, J. Phys. Soc. Jpn. **48**, 943 (1980).

[14] G. Bissinger, J. M. Joyce, R. Laubert, and S. L. Varghese, IEEE Trans. Nucl. Sci. **28**, 1149 (1981).

[15] In the celebrated paper (Ref. 1) Bragg and Kleeman, contrary to common supposition about the Bragg rule, state only that the stopping power of a complex molecule is *proportional* to the sum of stopping powers of the constituent atoms. They do in fact observe in their Fig. 3 a difference between elemental and molecular materials. The stopping powers shown in this figure also appear to have different proportionality constants for different molecules, in violation of the strict additivity rule.