

# Absolute Gross Ionization Cross Sections for Electrons (0.6–12 keV) in Hydrocarbons

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Measurements have been made of absolute gross ionization cross sections for 0.6–12 keV electrons in the following hydrocarbons: the series of alkanes from methane to hexane, a number of alkenes, butadiene, and benzene. A description of the experimental technique is given, the results are compared with those of other authors and the additivity of the cross sections is discussed.

In all cases the energy dependence of the cross sections is in agreement with the theoretical relation: the cross section  $\sigma$  is proportional to  $M^{1/2}E_{e1}^{-1} \ln E_{e1}$ , which gives a possibility of comparing with photoionization cross sections.

## I. INTRODUCTION

**D**ETERMINATION of absolute ionization cross sections of hydrocarbons (for rare gases: See Ref. 1) with the condensor technique is interesting in view of a comparison of their energy dependence with the theory, given by Miller and Platzman,<sup>2</sup> who also indicated in which way to relate these measurements to photoionization and absorption experiments.

Furthermore, from the extensive number of absolute values, presented in this work, it is easy to study the additivity of these cross sections in the series of alkanes and alkenes. Also, as our measuring technique does not have any mass discrimination, it is useful to make a comparison with various mass-spectrometrical measurements on the ionization products of these hydrocarbons.

Few investigators have determined absolute cross sections; we mention the work of Tate and Smith<sup>3</sup> and Tozer<sup>4</sup> and the photometrical results of Schoen,<sup>5</sup> Rustgi,<sup>6</sup> and Lukirsky, Brytov, and Zimkina.<sup>7</sup> Relative cross sections were measured by Otvos and Stevenson,<sup>8</sup> by Lampe, Franklin, and Field,<sup>9</sup> and by Kébarle and Godbole,<sup>10</sup> who normalized their values to the absolute ones of Smith.<sup>11</sup>

In the present report results are given for the absolute gross ionization cross sections (including multiple ionization and ionization of fragments) of 0.6–12 keV electrons impacting on the following hydrocarbons: CH<sub>4</sub>, CD<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, cyclo-C<sub>3</sub>H<sub>6</sub>, *n*-C<sub>4</sub>H<sub>10</sub>, *iso*-C<sub>4</sub>H<sub>10</sub>, *n*-C<sub>5</sub>H<sub>12</sub>, *neo*-C<sub>5</sub>H<sub>12</sub>, *iso*-C<sub>5</sub>H<sub>12</sub>, *n*-C<sub>6</sub>H<sub>14</sub>; C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, 1-C<sub>4</sub>H<sub>8</sub>, *trans*-2-C<sub>4</sub>H<sub>8</sub>, *cis*-2-C<sub>4</sub>H<sub>8</sub>, 1,3-C<sub>4</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>6</sub>.

<sup>1</sup> B. L. Schram, F. J. de Heer, M. J. van der Wiel, and J. Kistemaker, *Physica* **31**, 94 (1965).

<sup>2</sup> W. F. Miller and R. L. Platzman, *Proc. Phys. Soc. (London)* **A70**, 299 (1957).

<sup>3</sup> J. T. Tate and P. T. Smith, *Phys. Rev.* **39**, 270 (1932).

<sup>4</sup> B. A. Tozer, *J. Electron. Control* **4**, 149 (1958).

<sup>5</sup> R. I. Schoen, *J. Chem. Phys.* **37**, 2032 (1962).

<sup>6</sup> O. P. Rustgi, *J. Opt. Soc. Am.* **54**, 464 (1964).

<sup>7</sup> A. P. Lukirskii, I. A. Brytov, and T. M. Zimkina, *Opt. i Spektroskopiya* **17**, 438 (1964) [English transl.: *Opt. Spectry. (USSR)* **17**, 234 (1964)].

<sup>8</sup> J. W. Otvos and D. P. Stevenson, *J. Am. Chem. Soc.* **78**, 546 (1956).

<sup>9</sup> F. Lampe, J. L. Franklin, and F. H. Field, *J. Am. Chem. Soc.* **79**, 6129 (1957).

<sup>10</sup> P. Kébarle and E. W. Godbole, *J. Chem. Phys.* **36**, 302 (1962).

<sup>11</sup> P. T. Smith, *Phys. Rev.* **36**, 1293 (1930).

## II. EXPERIMENTAL

The apparatus and experimental technique are largely the same as those described in a previous article,<sup>1</sup> except some minor points which are discussed now.

### A. Pressure Measurements

The effect of mercury vapor streaming from the reservoir to the cold trap was prevented in our previous

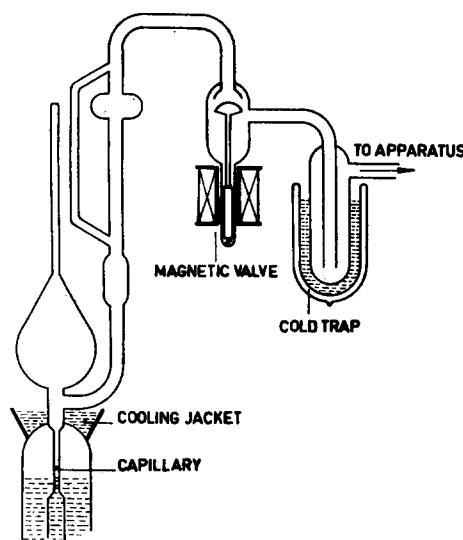


FIG. 1. Modified McLeod gauge.

experiment by means of a cooling jacket around the walls just above the reservoir; in the present work the same result—which was checked for argon—was attained by mounting a capillary (length 15 cm, diameter 2 mm) between the reservoir and the rest of McLeod gauge.<sup>12</sup> (See Fig. 1.)

Any possible effects that might occur in the time the mercury takes to pass the opening of the side tube of the McLeod, were eliminated by closing off the cold trap with a magnetic valve during that time (about  $\frac{1}{2}$  min). The cold trap was filled with an acetone-CO<sub>2</sub> mixture to prevent condensation of the hydrocarbons.

<sup>12</sup> C. Meinke and G. Reich, *Vakuum-Tech.* **11**, 86 (1962).

### B. Electron Source

Repeated discharges in the electron gun (Philips 6-AW-59 television gun), due to the very large ionization cross sections of the big hydrocarbon molecules, necessitated paying considerable attention to the insulation of the electron source and to increase the pumping speed at the gun compartment. After these improvements the gun could be operated normally, provided we did not take alkynes as target gases, as these seemed to poison the oxide cathode. The energy range of 0.6–12 keV was covered by two John Fluke High Voltage Supplies (Model 408 A/J).

### C. Evaluation of Measurements

A measurement of positive ionization current (on one of the condensor plates), the electron beam current, and the absolute gas pressure enables us to calculate the gross ionization cross sections from

$$\sigma = [I_+ / (I_- p 3.535 \times 10^{16})] (T/273) \quad (\text{cm}^2/\text{mole}),$$

where  $I_+$  is the positive ionization current,  $I_-$  is the electron beam current,  $l$  is the length of condensor plate in centimeters,  $p$  is the pressure in torricellis, and  $T$  is the temperature (which was taken to be room temperature) in Kelvin degrees. For the scattered fast electrons the same correction was applied as mentioned in Ref. 1.

As can be inferred from the formula of  $\sigma$ , the quotient  $I_+/I_-$  has to be linear with  $p$ ; deviation from linearity limited our pressure range to  $1\text{--}6 \times 10^{-4}$  Torr for the largest hydrocarbons.

### D. Disturbing Effects

#### 1. Collection of Slow Electrons

The collection of slow electrons (ejected from the gas molecules in the ionization process) in the beam collector is a result of the potential configuration, i.e., a potential hill in the condensor region. In the case of the largest hydrocarbons the Faraday-cage current was appreciably increased by this effect; therefore, after reading the ion current with the normal potential distribution, the potential of Electrodes 12 and 13 (see Ref. 1) was reversed and the real beam current—only fast electrons—was measured. The largest correction, for hexane, under the conditions: energy 0.6 keV, pressure  $6 \times 10^{-4}$  Torr, and magnetic field 400 G, amounted to 15%. This correction, which evidently is dependent on the magnetic field, is reduced to 5% at 150 G. That this effect is really caused by electrons, formed along the beam path in the ionization process, can be made plausible with the following consideration: under the circumstances described above we find, over a path length of 2.5 cm (the length of the measuring electrodes) a ratio of ion current to electron current equal to 6%. So if all electrons, formed in the last 6 cm before the

collector, would reach it, we can expect a 15% increase in the negative signal.

#### 2. Saturation Current

The saturation current of the ion collection has the form shown in Fig. 2; after a prolonged period of measuring, we sometimes noticed serious deviations from this form, accompanied by instabilities in the ion current. An explanation of this effect was found in the charging up of hydrocarbon deposits on the measuring electrodes; and indeed a regular cleaning proved sufficient to overcome these troubles.

#### 3. Energy Loss of Primary Electrons

From stopping power measurements Platzman<sup>13</sup> has evaluated a mean energy loss of about 30 eV—due to both excitation and ionization—per ionization process. Now, what chance has an electron of losing energy before it causes an ionization between the condensor plates?

Assuming that  $\sigma_1$  is the cross section before energy loss,  $\sigma_2$  is the cross section after energy loss,  $n$  is the number of molecules per cubic centimeter, and  $l_1$  is the distance between collimator and condensor plates, the fraction of electrons which lost energy on  $l_1$  equals  $\sigma_1 n l_1$ . Then the correction factor on the ion current is given by  $\{1 + n l_1 (\sigma_2 - \sigma_1)\}^{-1}$ .

We calculate this correction for the most unfavorable conditions: target gas  $n\text{-C}_6\text{H}_{14}$ , electron energy 0.6 keV, and the pressure  $6 \times 10^{-4}$  Torr:  $n = 2 \times 10^{18}$  mole/cm<sup>3</sup>,  $l_1 = 10$  cm,  $\sigma_1 = \sigma(600 \text{ eV}) = 8.9 \times 10^{-16}$  cm<sup>2</sup>/mole,  $\sigma_2 = \sigma(570 \text{ eV}) = 9.2 \times 10^{-16}$  cm<sup>2</sup>/mole (extrapolated value),  $\sigma_2 - \sigma_1 = 3 \times 10^{-17}$  cm<sup>2</sup>/mole. The correction then amounts to about 1%. The correctness of this calculation is proved by the pressure independence of the cross sections (in the chosen pressure range).

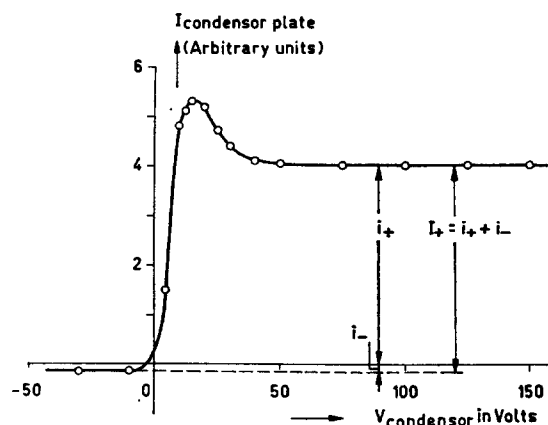


FIG. 2. Graph of the saturation current. (Target gas,  $n\text{-C}_4\text{H}_{10}$ ,  $E_{e1} = 10$  keV, and  $B = 160$  G).

<sup>13</sup> R. L. Platzman, Intern. J. Appl. Radiation Isotopes **10**, 116 (1961).

TABLE I. Ionization cross sections in  $10^{-16}$  cm<sup>2</sup>/mole.

Gas	keV					
	0.6	1	2	4	7	12
CH <sub>4</sub>	1.38	0.937	0.538	0.306	0.193	0.124
CD <sub>4</sub>	1.36	0.945	0.554	0.315	0.196	0.125
C <sub>2</sub> H <sub>6</sub>	2.83	1.93	1.12	0.630	0.400	0.255
cyclo-C <sub>3</sub> H <sub>6</sub>	3.41	2.28	1.32	0.745	0.470	0.300
C <sub>3</sub> H <sub>8</sub>	4.13	2.83	1.65	0.934	0.594	0.383
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	5.45	3.74	2.19	1.24	0.775	0.502
<i>iso</i> -C <sub>4</sub> H <sub>10</sub>	5.53	3.72	2.17	1.23	0.779	0.497
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	7.65	5.23	3.08	1.75	1.08	0.697
<i>iso</i> -C <sub>5</sub> H <sub>12</sub>	7.37	5.02	2.82	1.69	1.06	0.684
neo-C <sub>5</sub> H <sub>12</sub>	6.68	4.70	2.75	1.57	0.991	0.627
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	10.7	7.19	4.26	2.43	1.51	0.978
C <sub>2</sub> H <sub>4</sub>	2.31	1.58	0.921	0.517	0.335	0.207
C <sub>3</sub> H <sub>6</sub>	3.70	2.52	1.44	0.837	0.532	0.335
1-C <sub>4</sub> H <sub>8</sub>	5.65	3.61	2.11	1.20	0.749	0.471
<i>trans</i> -2-C <sub>4</sub> H <sub>8</sub>	5.25	3.56	2.06	1.16	0.731	0.459
<i>cis</i> -2-C <sub>4</sub> H <sub>8</sub>	5.65	3.78	2.20	1.28	0.781	0.490
1,3-C <sub>4</sub> H <sub>6</sub>	4.49	3.06	1.81	1.06	0.665	0.421
C <sub>6</sub> H <sub>6</sub>	7.83	5.37	3.12	1.77	1.11	0.698

#### 4. Secondary Ionization

Secondary ionization by electrons ejected from the target gas molecules need not be taken into consideration, even in the case of the largest hydrocarbons. We made a rough estimation of this effect on the basis of the number and the mean cross section of the ejected electrons and found a correction of about 2% in the case of *n*-C<sub>6</sub>H<sub>14</sub> at a pressure of  $6 \times 10^{-4}$  Torr.

### III. RESULTS

The gross ionization cross sections, listed in Table I, were evaluated in the same way as mentioned in the article by Schram *et al.*<sup>1</sup> The reproducibility of the cross sections is about 6%; apart from this random error, there is a systematical uncertainty, estimated to be 6%: 5% in the McLeod readings, due to unknown capillary and absorption effects; 1% in the absolute calibration of each tube voltmeter; 1% in the calibration of the electron energy. The gaseous hydrocarbons were taken from Phillips Company Ltd. gas cylinders; the purity claimed was better than 99.9%. In the case of liquid hydrocarbons (*n*-C<sub>5</sub>H<sub>12</sub>, *n*-C<sub>6</sub>H<sub>14</sub>, C<sub>6</sub>H<sub>6</sub>), we used "pro analysis" samples; a purity check on a mass spectrometer indicated a total contribution in ionization signal of about 1% from H<sub>2</sub>O and air, but no larger hydrocarbons.

The only direct comparison we can make is with the values of Kekarle and Godbole<sup>10</sup> (see Fig. 3) who normalized their results on the absolute ones of Smith.<sup>11</sup> The large discrepancy between their values and ours might be explained by two facts.<sup>14</sup> Firstly, they as-

sumed their total ion current to be the sum of all fragment ion currents at the collector of the mass spectrometer. But of all ions, which got some extra kinetic energy in the fragmentation process, only a very small fraction appears at the collector. Secondly, they evaluated their pressure from a measurement on the high-pressure side of a molecular leak. Although for noble gases the pressure ratio across the leak will be

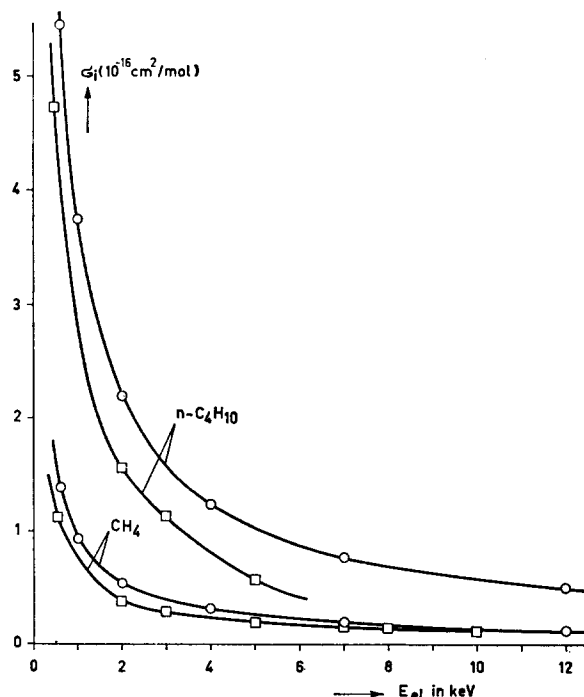


FIG. 3. Comparison of our work (O) with that of Kekarle and Godbole (□).

<sup>14</sup> The authors are indebted to Professor Kekarle for a helpful discussion on these points and for sending us the numerical values of his cross sections.

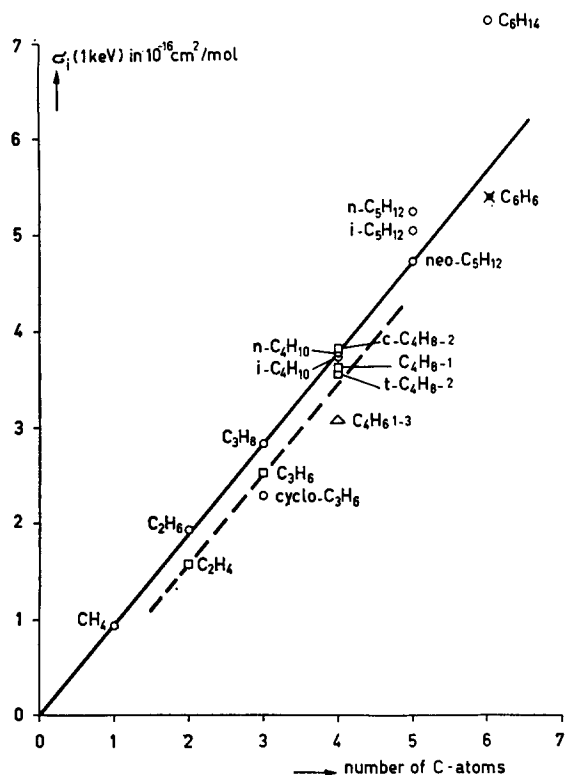


FIG. 4. Ionization cross sections of hydrocarbons for electrons of 1 keV against the number of C atoms (O, alkanes and  $\square$ , alkenes).

fairly constant, for the large hydrocarbons, with their high rate of adsorption, there might well have been a decrease of this ratio.

#### IV. ADDITIVITY OF CROSS SECTIONS

It is interesting to make a plot of the cross sections for instance at 1 keV against the number of C atoms (see Fig. 4). From this figure we try to prove the additivity of partial cross sections for the three types of bonding in the hydrocarbons (see Table II).

##### 1. (C-H) Bond

The values of  $\text{CH}_4$  represent four of these bonds, i.e., we can derive a value for the partial cross section of the (C-H) bond.

##### 2. $\sigma(\text{C-C})$ Bond

The series of alkanes appear to be straight lines, going through the origin (the values of  $n\text{-C}_5\text{H}_{12}$  and  $n\text{-C}_6\text{H}_{14}$  excepted; this deviation might be caused by some unknown adsorption phenomena<sup>15</sup>—either in the

gas-inlet system or the pressure gauge—resulting in a possible pressure difference between collision chamber and McLeod). The difference between two successive alkanes consists of the contributions of one  $\sigma(\text{C-C})$  bond plus two (C-H) bonds. This yields a value for the  $\sigma(\text{C-C})$  bond.

##### 3. $\pi(\text{C-C})$ Bond

A partial cross section for this bond can be evaluated from the difference between an alkane and the corresponding alkene (or dialkene, in the case of 1,3- $\text{C}_4\text{H}_6$ ). Only *cis*-2- $\text{C}_4\text{H}_6$  does not show the expected difference with the saturated butanes. We can check the applicability of these cross sections by means of a calculation of the total cross section for  $\text{C}_6\text{H}_6$ , considered as having three  $\pi(\text{C-C})$  bonds, which yields 4.74; the agreement with the experimental value of 5.37 is reasonable, especially in view of the random error of 6%. The straight line for the cross sections of alkanes can also be found in the low-energy work of Otvos and Stevenson<sup>8</sup> (75-eV electrons in a mass-spectrometer source) and of Schoen<sup>5</sup> (photons up to 25 eV), whose values at the ionization maximum—about 16 eV—give a straight line.

#### V. RELATION WITH PHOTOIONIZATION MEASUREMENTS

On the basis of the Bethe-Born approximation, the total ionization cross section can be represented in our energy range by<sup>2</sup>

$$\sigma = (4\pi a_0^2 R / E'_{e1}) M_I^2 \ln c_i E'_{e1},$$

where  $a_0$  is the first Bohr radius of atomic hydrogen,  $R$  the Rydberg energy,  $E'_{e1}$  the electron energy, corrected for relativistic effects ( $E'_{e1} = \frac{1}{2} m_0 v^2$ ), and  $M_I^2$  and  $c_i$  are constants. The quantity  $M_I^2$  is related to the differential oscillator strength  $df/dE$  by<sup>2</sup>

$$M_I^2 = \int_{\text{I.P.}}^{\infty} \frac{df}{dE} \frac{R}{E} dE. \quad (1)$$

In the case of molecules a complication arises due to the so-called superexcited states (states with excitation energy exceeding the ionization energy), which will decay either by pre-ionization or by dissociation. This

TABLE II. Partial cross sections for the three types of bonding in the hydrocarbons.

Type of bonding	$\sigma(1 \text{ keV})$ in $10^{-16} \text{ cm}^2$	$\sigma(12 \text{ keV})$ in $10^{-16} \text{ cm}^2$
C-H	0.24	0.031
$\sigma(\text{C-C})$	0.47	0.064
$\pi(\text{C-C})$	0.18	0.014

<sup>15</sup> P. H. Carr, *Vacuum* **14**, 37 (1964).

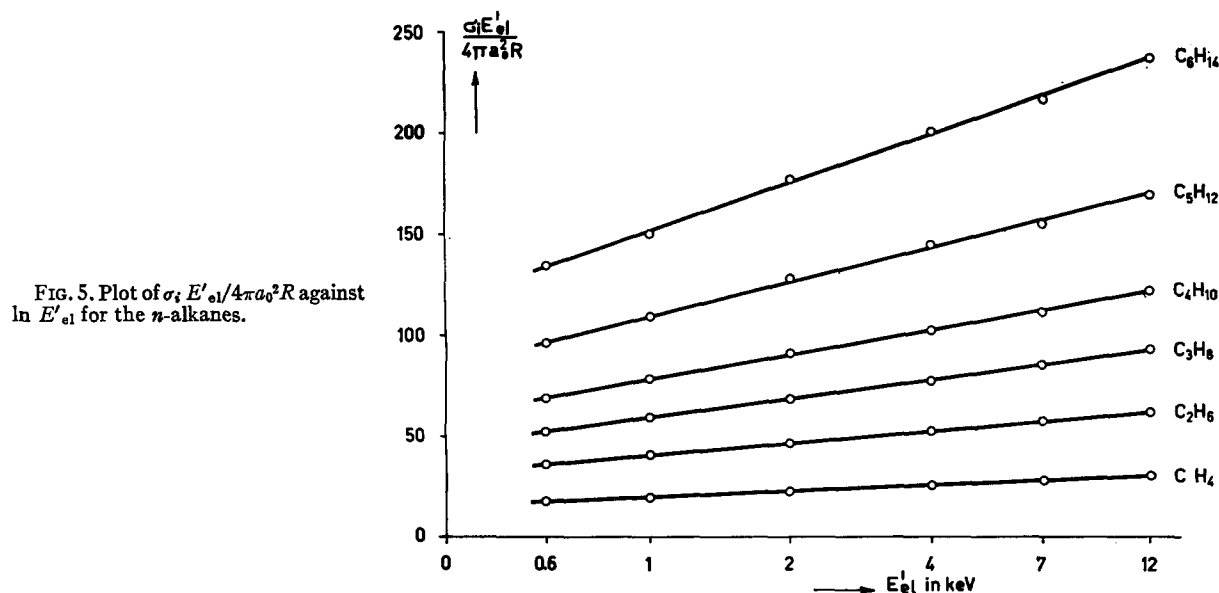


FIG. 5. Plot of  $\sigma_i E'_{ei}/4\pi a_0^2 R$  against  $\ln E'_{ei}$  for the  $n$ -alkanes.

can be taken into account by adding a factor  $\eta(E)$ , denoting the efficiency of ionization when the molecule has acquired an energy  $E$ , and we get, consequently,

$$M_i^2 = \int_{I.P.}^{\infty} \eta(E) \frac{df}{dE} \frac{R}{E} dE = \bar{\eta} \int_{I.P.}^{\infty} \frac{df}{dE} \frac{R}{E} dE = \bar{\eta} M_I^2.$$

In Fig. 5 we have plotted  $\sigma_i E'_{ei}/4\pi a_0^2 R$  versus  $\ln E'_{ei}$  for all the  $n$ -alkanes. Obviously, for each compound the cross sections satisfy the theoretical relation, the deviation of each point from the straight line being less than 2%. Similar graphs were made for the remaining hydrocarbons, all of which showed the same behavior. The values of  $M_i^2$  and  $c_i$ , calculated from a least-squares analysis from the slopes  $M_i^2$  and the intercepts  $M_i^2 \ln c_i$ , are listed in Table III.

By means of the relation between the oscillator strength and the photoionization cross section we can rewrite (1) into:

$$M_i^2 = \frac{mcR}{\pi e^2 h} \int_{I.P.}^{\infty} \frac{\sigma_{ph}(E)}{E} dE.$$

The values of  $M_i^2$  calculated in this way are included in Table III. For most hydrocarbons—CH<sub>4</sub> excepted<sup>6,7</sup>—the photoionization cross sections have been measured only up to 25 eV, which is a rather low upper limit for an integration over the whole continuum. But, by plotting the results of Schoen<sup>5</sup> on a linear wavelength scale and extrapolating to zero wavelength, we made a rough estimate of the contributions of transitions to higher-energy states.

In the same way as we did with the cross sections, we can determine the additive character of  $M_i^2$  (see Fig. 6) and calculate the partial contribution for the various types of bonding. The result is for the C-H

TABLE III. Values of  $M_i^2$  and  $c_i$ .

Gas	$M_i^2$	$c_i$ in eV <sup>-1</sup>	$M_i^2$
	This work		Photo-ionization
CH <sub>4</sub>	4.28	0.094	4.2 <sup>a</sup>
CD <sub>4</sub>	4.73	0.060	
C <sub>2</sub> H <sub>6</sub>	8.63	0.107	6.1 <sup>b</sup>
cyclo-C <sub>3</sub> H <sub>8</sub>	10.2	0.109	8.1
C <sub>3</sub> H <sub>8</sub>	13.8	0.071	7.5
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	17.8	0.080	12.2
<i>iso</i> -C <sub>4</sub> H <sub>10</sub>	17.4	0.089	
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	24.4	0.088	
<i>iso</i> -C <sub>5</sub> H <sub>12</sub>	25.0	0.064	
neo-C <sub>5</sub> H <sub>12</sub>	23.0	0.069	
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	34.8	0.078	
C <sub>2</sub> H <sub>4</sub>	7.32	0.091	5.1
C <sub>3</sub> H <sub>6</sub>	12.0	0.080	
1-C <sub>4</sub> H <sub>8</sub>	15.3	0.156	
<i>trans</i> -2-C <sub>4</sub> H <sub>8</sub>	15.5	0.120	
<i>cis</i> -2-C <sub>4</sub> H <sub>8</sub>	16.7	0.120	9.5
1,3-C <sub>4</sub> H <sub>6</sub>	15.9	0.058	7.1
C <sub>6</sub> H <sub>6</sub>	24.2	0.102	

<sup>a</sup> See Refs. 6 and 7.

<sup>b</sup> See Ref. 5 for remaining entries in this column.

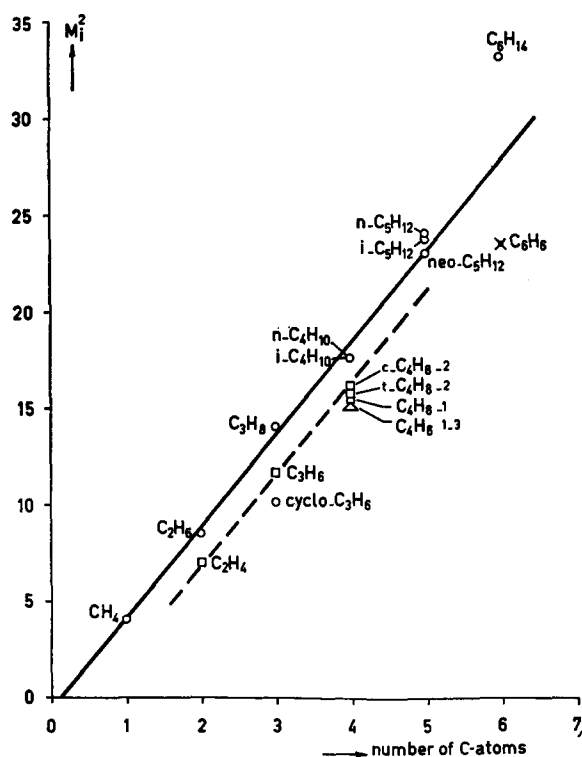


FIG. 6. Values of  $M_i^2$  for hydrocarbons against the number of C atoms (○, alkanes and □, alkenes).

bond, 1.07, for the  $\sigma$ (C-C) bond, 2.5, and for the  $\pi$ (C-C) bond, 0.4. So it appears from the present experiment that the ionization of a  $\sigma$  electron has a greater probability than that of a  $\pi$  electron. Probably the greater part of the transitions in which  $\pi$  electrons are involved, are leading to discrete levels. This conclusion is supported by photoelectron spectroscopic work on ethylene<sup>16</sup> and acetylene.<sup>17</sup> Although a direct comparison with our results is impossible, as the quantity  $M_i^2$  requires an integration over the whole continuum, the general trend seems to be the same.

#### ACKNOWLEDGMENTS

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<sup>16</sup> M. I. Al-Joboury and D. W. Turner, J. Chem. Soc. **1964**, 4434.

<sup>17</sup> M. I. Al-Joboury, D. P. May, and D. W. Turner, J. Chem. Soc. **1965**, 616.