

takes place in irradiated D<sub>3</sub>-glycine.

Whereas the exchange reactions between radical and host molecules were very slow in  $\alpha$ -alanine (several years at 20°, 3 hr. at 150° for complete conversion), reactions 1 and 2 in irradiated glycines must be very fast since the postulated "initial" radicals were not observed.

It would therefore appear that caution must be exercised in the identification of radicals as a result of deuteration studies.

**Acknowledgments.**—The author gratefully thanks Commercial Products Division, Atomic Energy of Canada Ltd., for the use of their irradiation facilities. Thanks are also extended to Drs. A. Horsfield and D. H. Whiffen for helpful correspondence.

[CONTRIBUTION FROM THE RESEARCH DIVISION, ALLIS-CHALMERS MFG. CO., MILWAUKEE, WIS.]

## Partial Ionic Character of Diatomic Molecules

BY RAYMOND P. ICZKOWSKI

RECEIVED AUGUST 16, 1963

The partial ionic character of a diatomic molecule is derived from a semiclassical model. Total bond energy is treated as a sum of ionic and covalent contributions. The ionic component is a sum of coulombic, polarization, and partial ionization energies. Covalent energy is calculated by a generalization of Mulliken's method. The fractional ionic character is the value at which the total energy is a minimum. Application of the method to BrCl, ClF, BrF, and NaCl yields values of ionic character in rough agreement with values obtained from nuclear quadrupole coupling constants.

### Introduction

Recently, relationships between electronegativity and partial ionic character have been formulated in terms of the concept of equalization of electronegativity.<sup>1</sup> As shown in Table I, this method yields values of percentage ionic character lower than the experimental values obtained from nuclear quadrupole coupling constants.<sup>2</sup> An alternative to this theory would be to derive the partial ionic character from a semiclassical model of a diatomic molecule. In a classical treatment of two oppositely charged spheres separated by an anharmonic nonconducting spring, the total energy of the system could be considered as a sum of the energy of compression of the spring plus the electrostatic energy of the two charged spheres. In this paper, the bond energy of a partially ionic molecule is considered as a sum of separate contributions due to the electrostatic energy and the energy of covalent binding.

has the effect of multiplying the electrostatic attraction by the term

$$\left[ 1 + \frac{\alpha_A + \alpha_B}{2r_0^3} + \frac{2\alpha_A\alpha_B}{r_0^6} \right]$$

where  $\alpha_A$  is the polarizability of atom A. It was shown in a previous paper<sup>4</sup> how the energies of partial ionization  $E_A(-N)$  and  $E_B(N)$  could be evaluated from a plot of the total energies of atoms A and B as a function of degree of ionization. The polarizability also depends on the degree of ionization; e.g., for the molecule ClF,  $\alpha_F$  would be intermediate between the values for F and F<sup>-</sup>, and  $\alpha_{Cl}$  would be intermediate between the values for Cl and Cl<sup>+</sup>. The dependence of the polarizability on degree of ionization has been shown<sup>5</sup> to be of the form: constant  $\times n^6/Z^4$ , where  $n$  is the principal quantum number of the outermost electrons and  $Z$  is the effective nuclear charge.

TABLE I

	ClF	BrF	BrCl	LiBr	NaBr	KCl	KBr	RbCl	CsCl
% ionic character									
From equalization of electronegativity	9.86	13.4	8.15	39.4	40.9	48.9	46.1	50.0	52.0
From nuclear quadrupole coupling	25.9	32.9	5.6 or 11.0	94.4	91.1	100	98.5	99.2	96.8

### Ionic and Covalent Components of the Bond Energy.

—The ionic contribution,  $E_i(N)$ , at fractional ionic character  $N$  of a molecule AB, is easily calculated as a sum of four parts: (1) the energy  $E_A(-N)$  required to remove a fraction of an electronic charge,  $Ne$ , from atom A; (2) the energy  $E_B(N)$  required to place this charge on atom B; (3) the energy  $-(Ne)^2/r_0$  due to the electrostatic attraction between two atoms of charge  $Ne$  separated by the internuclear distance  $r_0$ ; (4) a correction<sup>3</sup> for polarization, i.e., the distortion of the electron clouds due to the electrostatic attraction. Polarization

According to Mulliken,<sup>6</sup> the energy of a covalent bond can be found from a semitheoretical formula which is a quantitative extension of the Slater-Pauling theory of maximum overlap. According to Mulliken's method this bond energy in a molecule is given by an attractive contribution  $-AIS/(1+S)$  due to electrons from each atom, which are paired in the molecule, together with a sum of repulsive contributions of the form:  $1/2m_A m_B \gamma AIS^2$  due to electrons from different atoms which are not involved in a bond; where  $\gamma = 0.7$ ,  $A = 1.16$  for  $\sigma$ -orbitals and 1.53 for  $\pi$ -orbitals,  $I$  is the average ionization energy of the two orbitals

(1) J. Hinze, M. A. Whitehead, and H. H. Jaffé, *J. Am. Chem. Soc.*, **85**, 148 (1963); H. O. Pritchard, *ibid.*, **85**, 1876 (1963); R. Ferreira, *Trans. Faraday Soc.*, **59**, 1064, 1075 (1963); R. T. Sanderson, *J. Am. Chem. Soc.*, **74**, 272 (1952); *Science*, **114**, 670 (1951).

(2) B. P. Dailey and C. H. Townes, *J. Chem. Phys.*, **23**, 118 (1955).

(3) E. S. Rittner, *ibid.*, **19**, 1030 (1951).

(4) R. P. Iczkowski and J. L. Margrave, *J. Am. Chem. Soc.*, **83**, 3547 (1961).

(5) L. Pauling, *Proc. Roy. Soc. (London)*, **A114**, 191 (1927).

(6) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

TABLE II  
IONIC CONTRIBUTION TO BOND ENERGY

$N$	0	0.2	0.4	0.6	0.8	1
$E_{Cl}(-N)$ , e.v.	0	2.19	4.80	7.81	11.23	15.00
$E_F(N)$ , e.v.	0	-2.18	-3.65	-4.38	-4.18	-3.64
$\alpha_{Cl}(-N)$ , Å. <sup>3</sup>	2.06	1.92	1.77	1.65	1.52	1.42
$\alpha_F(N)$ , Å. <sup>3</sup>	0.49	0.54	0.58	0.63	0.69	0.76
$-\frac{N^2}{r_e} \left\{ 1 + \frac{\alpha_F + \alpha_{Cl}}{2r_e^3} + \frac{2\alpha_F\alpha_{Cl}}{r_e^6} \right\}$	0	-0.49	-1.95	-4.38	-7.75	-12.10
$E_F(N) + E_{Cl}(-N)$ , e.v.	0	0.01	1.15	3.43	7.05	11.36
$E_i(N)$ , e.v.	0	-0.48	-0.80	-0.95	-0.70	-0.74

involved, and  $n_A$  is the number of electrons in the orbital on A. As an illustrative example, if LiH were considered to be completely ionic, the covalent repulsion between the two closed shells on the  $Li^+$  and  $H^-$  ions would be  $2\gamma AIS^2$ . If LiH were completely covalent, the repulsive energy between the  $(1s)^2$  shell of Li and the electron from H which forms the bond would be  $\gamma AIS^2$ . In this paper, Mulliken's formula will be extended to partially ionic bonds, and  $n$ , the number of electrons on an atom, will be assumed to take on fractional as well as integral values. Thus, if LiH is 80% ionic, then the 2s electron originally from Li spends 80% of its time around the H nucleus and 20% of its time around the Li nucleus. Therefore, there will be an interaction of two electrons from the 1s orbital of Li with 1.8 electrons from 1s of H, and the energy of repulsion will be  $1.8\gamma AIS^2$ .

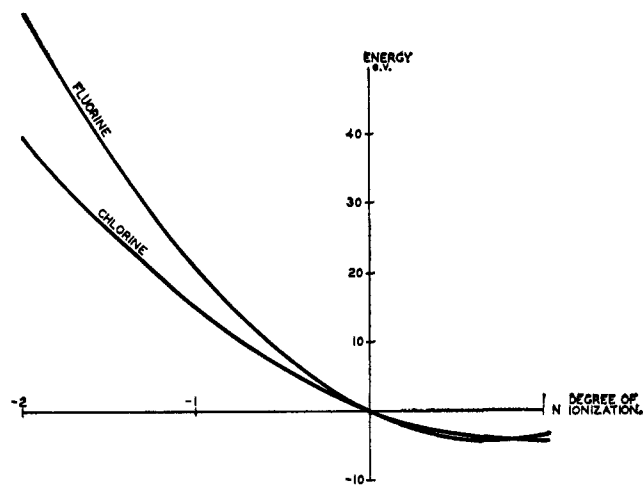


Fig. 1.—Energies of atoms as a function of degree of ionic character.

One pair of electrons are involved in the bond between 1s of H and 2s of Li. However, the overlap integral is supplemented by the effect of the decreased electron density around Li and the increased electron density around H. The molecular bonding orbital in a partially ionic molecule involves nonequal contributions from the two heteroatoms

$$\psi = a\varphi_{Li} + b\varphi_H$$

where  $\varphi_{Li}$  is the 2s orbital of Li, and  $\varphi_H$  is the 1s orbital of H. Squaring and integrating both sides of the equation yields

$$1 = a^2 + b^2 + 2abS$$

where  $S$  is the overlap integral between 2s of Li and 1s of H. The last term is the one responsible for the covalent bond. Therefore,  $S$  is replaced by  $abS$  in the

formula for the attractive contribution to the bond energy:  $-AIabS/(1 + abS)$ . Since  $a^2 \approx 1 - N$  and  $b^2 \approx 1 + N$ , the strength of the bond becomes

$$-AI \frac{\sqrt{1 - N^2}S}{1 + \sqrt{1 - N^2}S}$$

The degree of hybridization is chosen so as to minimize the total covalent energy of the molecule.

Two other effects which must be taken into account are: As electrons are transferred from atom A to atom B the other electrons on A experience less shielding of the nuclear charge and, therefore, the effective nuclear charge for electrons in the same shell increases by  $0.35 \cdot N$ . The energy of promotion to the proper valence state must be subtracted from the total calculated bond energy.

The total energy of a molecule at any partial ionic character,  $N$ , will be the sum of the ionic and covalent energies at that value of  $N$

$$E(N) = E_i(N) + E_c(N)$$

Because all mechanical systems tend to go to the state of lowest energy, the fractional ionic character and the dissociation energy of the molecule are given by the values of  $N$  and  $E$  at which  $E(N)$  has a minimum. This treatment rests on the assumption that an atom in a molecule can have ascribed to it a total energy and a polarizability for nonintegral as integral values of the electronic charge and that Mulliken's formula holds for such partially ionized atoms.

**Application of the Theory of CIF.**—As a test of the theory, the fractional ionic character and dissociation energy of CIF were calculated.

The graphs in Fig. 1 show how the total energy of the atoms F and Cl change as charge is added to or subtracted from them.<sup>4</sup> In these graphs, the energy of the neutral atom,  $E(0)$ , is taken as zero; the energy of  $F^-$  is  $E(+1)$  and is equal to the electron affinity; the energy of  $F^+$  is  $E(-1)$  and is equal to the first ionization potential;  $E(-2)$  is the energy of  $F^{+2}$  and is equal to the sum of the first and second ionization potentials, etc.

Table II gives the value of the ionic contributions to the bond energy at various values of the partial ionic character. Table III gives some of the data used to calculate the covalent contribution. The effective nuclear charges were evaluated for different amounts of fractional ionic character. From these, the overlap integrals were evaluated by interpolation from Mulliken's tables.<sup>7</sup> The ionization potential at any value of  $N$  is given by  $E(N) - E(N - 1)$  and was found from the energy curves in Fig. 1. Table IV gives the formu-

(7) R. S. Mulliken, *J. Chem. Phys.*, **17**, 1248 (1949).

TABLE III  
COVALENT CONTRIBUTION TO BOND ENERGY

N	0	0.2	0.4	0.6
ZF	5.20	5.13	5.06	4.99
ZCl	6.10	6.17	6.24	6.31
S(2pσF, 3pσCl)	0.2608	0.2590	0.2580	0.2572
S(2pσF, 3sCl)	.1592	.1632	.1672	.1710
S(2sF, 3pσCl)	.2600	.2595	.2585	.2575
S(2sF, 3sCl)	.1762	.1770	.1780	.1782
S(2pπ, 3pπ)	.0760	.0770	.0775	.0782
Fluorine: $I_{2p\sigma} = I_{3p\pi}$ , e.v.	20.88	17.44	13.99	10.54
$I_{2s}$ , e.v.			41.80	
Chlorine: $I_{3p\sigma} + I_{3p\pi}$ , e.v.	15.08	17.00	18.91	20.83
$I_{2s}$ , e.v.			26.96	
Promotion energy, e.v.	0.06	0.47	0.88	1.29
s,p-Hybridization in F, %	4.4	2.3	1.0	0.5
s,p-Hybridization in Cl, %	4.8	7.3	10.9	14.4
Covalent energy ( $-E_c$ ), e.v.	1.86	1.55	1.13	0.70

las for the covalent energy contributions of the 2p and 2s orbitals of fluorine with the 3p, 3s, 2p, and 2s orbitals of chlorine. Interactions of other pairs of orbitals are too small to affect the bond energy appreciably.

TABLE IV  
COVALENT ENERGY CONTRIBUTIONS FROM ORBITALS

F-Orbital	Cl-Orbital	Expression for the energy
$h_{2p\sigma}$	$h_{3p\sigma}$	$-AI(1 - N^2)^{1/2}S/[1 + (1 - N^2)^{1/2}S]$
	$h_{3s, 2p\sigma, \text{ or } 2s}$	$\gamma AI(1 + N^2)S^2$
$h_{2s}$	$h_{3p\sigma}$	$\gamma AI(1 - N^2)S^2$
	$h_{3s, 2p\sigma, \text{ or } 2s}$	$2\gamma AIS^2$
$22p\pi$	$3p\pi$	$2\gamma A\pi IS^2$

Figure 2B shows the molecular energy and its components as a function of the fractional ionic character of ClF, considered as a variable. The electrostatic energy,  $\frac{(eN)^2}{r_e} \left[ 1 + \frac{\alpha_F + \alpha_{Cl}}{2r_e^3} + \frac{2\alpha_F\alpha_{Cl}}{r_e^6} \right]$ , is shown as  $E_{\text{elect}}$ . The true fractional ionic character and dissociation energy are given by the value of  $N$  and  $E$  at which the total energy curve has a minimum, which in this case is approximately 0.25 and 2.03 e.v. The calculated value of  $E$  at  $N = 0$  is 1.86 e.v. The experimental points, 2.616 e.v. at  $N = 0.26$  and 2.03 e.v. at  $N = 0$ , are also shown; according to Pauling,<sup>8</sup> the latter quantity is equal to the average of the dissociation energies of  $\text{Cl}_2$  and  $\text{F}_2$ . Similar calculations were performed for BrCl, BrF, and NaCl, except that more accurate values were used for the effective nuclear charge.<sup>9</sup> The results, shown in Fig. 2A, 2C, and 2D yield values of fractional ionic character 0.02, 0.35, and 0.75 for BrCl, BrF, and NaCl, respectively. Observed values<sup>2</sup> are 0.08, 0.33, and 0.93.

### Discussion

The calculated curves exhibit the expected minima, and are in agreement with experimental values, except for NaCl, which is too low by 18%. The error in NaCl arises partly from an overestimation of the covalent energy from Mulliken's formula and also from not taking into account the deformation of the orbitals by the high molecular electric field and the resulting effect on the covalent energy. The calculation of the covalent energy could probably be improved if the formulas were modified to include coulomb as well as overlap integrals.<sup>10</sup>

(8) L. Pauling, *J. Am. Chem. Soc.*, **54**, 3570 (1932).

(9) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

(10) R. S. Mulliken, *Rev. Mod. Phys.*, **32**, 254 (1960).

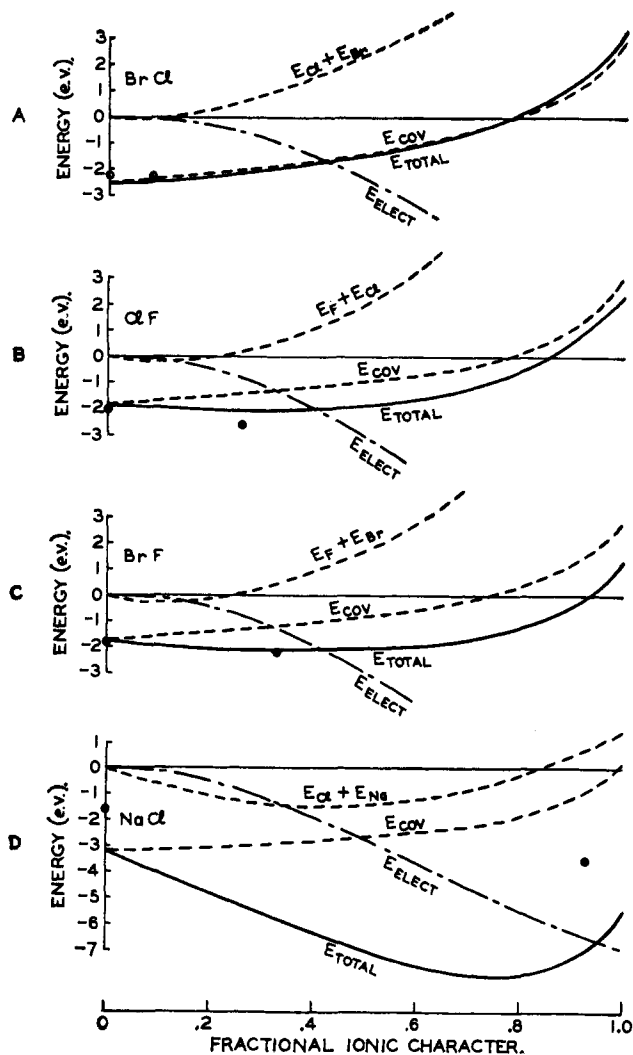


Fig. 2.—Total molecular energy as a sum of covalent, electrostatic, and partial ionization energies.

In the present treatment, the energy of the molecule is the sum of the *partially* covalent energy and the *partially* ionic energy. It differs from the quantum mechanical treatment<sup>11</sup> in which the energy of the molecule is a function of the *purely* covalent energy, the *purely* ionic energy, and the resonance energy. Like the method of "equalization of electronegativity," the present method has only approximate quantitative value; however, it provides an understanding of partial ionic character in terms of intuitive concepts.

Recently, computer programs based on the extended LCAO method have been developed, which can produce accurate SCF-MO wave functions for diatomic molecules. Mulliken<sup>12</sup> has shown that the partial ionic character of a molecule can be derived from such wave functions by means of an electronic population analysis.<sup>13</sup> He has also pointed out that (except for the homopolar case) the definition of the term "partial ionic character" is arbitrary to a certain extent.<sup>14</sup> The concept of partial ionic character arose within the framework of the classical view of a molecule as a combination of its constituent atoms. This concept probably does not have a precisely definable

(11) K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, Inc., New York, N. Y., 1953, p. 145.

(12) R. S. Mulliken, *J. Quant. Spectry. Radiative Transfer*, **2**, 415 (1963).

(13) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

(14) R. S. Mulliken, *ibid.*, **36**, 3428 (1962).

quantum mechanical analog because according to the latter view, "a molecule is something new and different from an additive combination of atoms."<sup>14</sup> In this

respect, partial ionic character has approximately the same usefulness and validity as the concept of atomic radii.

[CONTRIBUTION FROM THE NUCLEAR CHEMISTRY DEPARTMENT, SOREQ RESEARCH ESTABLISHMENT, ISRAEL ATOMIC ENERGY COMMISSION, YAVNE, ISRAEL]

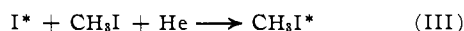
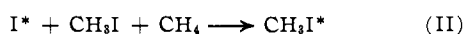
## Selectivity Effects in Recoil Labeling of Methyl Iodide by Fission-Produced Iodine

BY YEHUDA PAISS<sup>1</sup> AND SAADIA AMIEL

RECEIVED DECEMBER 14, 1963

Recoil labeling of methyl iodide by fission-produced iodine isotopes was observed to be of higher efficiency with independently produced iodine than of the same isotopes recoiling after  $\beta$ -decay.

A study is being made of the formation of radioactive methyl iodide by the recoil of fission-produced iodine isotopes into methane, methyl iodide, and mixtures of methyl iodide with different gases. We have measured the isotope composition of the iodine in labeled methyl iodide formed in the reactions



Plastic irradiation containers ("rabbits") in which the interior was coated with a layer of  $\sim 2$  mg./cm.<sup>2</sup> uranium were filled with the corresponding gases and irradiated in the neutron flux of the Israel Research Reactor IRR-1. The gas, in which a substantial quantity of the recoiling fission products of the uranium was stopped, was then extracted from the container and the methyl iodide was separated from the other gases by gas chromatography. Various gas chromatography columns were used and found adequate, the best being a 100-cm. column of 25% silicone fluid No. 702 on Sil-o-Cel firebrick of 50-70 mesh at 70°, with a flow rate of 80 ml./min. The CH<sub>3</sub>I peak appeared after 1.5 min. The radioactivity of the methyl iodide fraction was analyzed with a scintillation spectrometer connected to a multichannel pulse height analyzer.

The  $\gamma$ -ray spectra of the purified fractions of methyl iodide from different sources disclosed differences in the relative yields of the radioactive iodine isotopes. Table I gives representative results for the ratio of I<sup>135</sup> to

I<sup>136</sup> and I<sup>133</sup> is then  $\geq 7.2$ . If the ratio of the cumulative yields of these isotopes is taken as unity (it is actually 0.92), as presented in Table I, the ratio of the independent yields is  $\geq 7.8$ .

The results shown in the table point to the occurrence of a process in which the formation of labeled methyl iodide by recoil is of higher efficiency when the recoiling iodine is produced independently, *viz.*, as a fission fragment, rather than when the iodine results from  $\beta$ -decay of its precursors.

A recent experiment<sup>3</sup> in which fission recoils were stopped in methane showed marked differences in the distribution of iodine isotopes in the gas as compared with the distribution on a negatively charged collector. It was indicated that the abundance of I<sup>135</sup> compared to I<sup>133</sup> was greater in the gaseous phase in which the radioactive iodine is believed to be mainly in the form of CH<sub>3</sub>I.

Since all recoils resulting from  $\beta$ -decay are charged,<sup>4</sup> while primary fission fragments near the end of their range are not,<sup>5</sup> electric collection will be mainly effective with  $\beta$ -decay products, and it is thus to be expected that a fraction of fission products extracted electrostatically from the stopping gas will be enriched to a certain extent with  $\beta$ -decay products, or rather, depleted with respect to primary fission fragments. Hence, the effect observed in ref. 3, although very similar to that reported in this paper, can be attributed to *electrostatic fractionation* which is expected *a priori*, rather than to *selective labeling* of the gas. In addition, the form of the labeled gaseous compound has not been investigated experimentally.

Thus, to demonstrate unambiguously that selective labeling in methyl iodide does take place, it is a prerequisite to isolate the CH<sub>3</sub>I from the stopping gas and compare the distribution of iodine isotopes in it with an *undisturbed* pattern of cumulative yields of iodine isotopes from fission.

The indication of the occurrence of selective labeling is in general agreement with the model<sup>6</sup> pointing at kinetic energy considerations as criteria for discrimination and selectivity in replacement reactions, like the ones studied in the present work.

(2) S. Katcoff, *Nucleonics*, **18**, No. 11, 201 (1960).

(3) H. O. Denschlag, N. Henzel, and G. Herrmann, *Radiochim. Acta*, **1**, 172 (1963).

(4) T. A. Carlson, A. H. Snell, F. Pleasonton, and C. H. Johnson, *Proceedings of the Symposium on Chemical Effects of Nuclear Transformations*, Prague, 1960, pp. 155-160; IAEA, Vienna, 1961.

(5) G. N. Walton, *Progr. Nucl. Phys.*, **6**, 193 (1957).

(6) S. Amiel and Y. Paiss, "Criteria for Selectivity in Recoil Labeling," Israel AEC Report IA-907 (in print).

TABLE I  
RATIOS OF I<sup>135</sup>/I<sup>133</sup> FROM DIFFERENT SOURCES

Reaction	I <sup>135</sup> /I <sup>133</sup> <sup>b</sup>
Iodine from U <sup>235</sup> (n,f)	1.0
I* + CH <sub>4</sub> (760) <sup>a</sup>	1.5-2.0
I* + CH <sub>3</sub> I (300) + CH <sub>4</sub> (460)	2.5-5.0 <sup>c</sup>
I* + CH <sub>3</sub> I (300) + He (460)	$\sim 5$

<sup>a</sup> Indicated pressures are partial, in mm. <sup>b</sup> The error in each measurement of CH<sub>3</sub>I is  $\pm 25\%$ . <sup>c</sup> For short irradiations (1 min. or less) the ratios are close to 5, and for longer irradiations ( $\geq 10$  min.) they are closer to 2.5.

I<sup>133</sup>, as obtained from recoil labeling of a few gas mixtures, compared with the ratio of the same isotopes extracted from uranium irradiated and separated under the same time conditions.

It should be noted that I<sup>135</sup> is formed in fission with a greater independent fission yield (2.37%) than I<sup>133</sup> (<0.33%).<sup>2</sup> The ratio of the independent yields of

(1) Part of a study leading to a Ph.D. degree.