TABLE I.[a]

	(1) Process		(2) Relative abundance percent[b]	(3) $Q_a'f_2{}^c$
(1)	$CH_4{}^+$	$CH_3{}^+$	0.05	(5)[d]
		$CH_2{}^+$	0.008	0.74
		CH^+	0.001	0.096
		C^+	0.0003	0.033[e]
(2)	$CH_3{}^+$	$CH_2{}^+$	0.0074	(0.7)[d]
		CH^+	0.0025	0.31
		C^+	0.0004	0.057[e]
(3)	$CH_2{}^+$	CH^+	...	...
		C^+	...	(0.12)[e]
(4)	CH^+	C^+	...	(0.42)[e]

[a] All figures in this table are obtained from the measured peak heights.
[b] Abundance relative to the primary ion intensities of $CH_4{}^+$ and $CH_3{}^+$ equal 100 respectively, calculated from Rosenstock+Melton's data.
[c] In units $cm^2/cm^2/mm$ Hg.
[d] Estimated from relative abundance of this ion according to Rosenstock and Melton (col. 2).
[e] Estimated from relative abundance of this ion in our spectra at one pressure only.

occur in a much more important fraction of the ions lost in the tube (4%) than would appear at first sight from the relative abundance values (0.05%, Table I, column 2). Taking the above-mentioned corrections into account, it may be assumed that dissociation and charge exchange for $CH_4{}^+$ in CH_4 are of approximately equal importance: this result is in agreement with Lindholm's observation[6] with 500 ev ions.

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Possibility of Enhanced Catalytic Reactions

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IN a recent paper[1] we have described experiments on the enhancement of rate and extent of gas-solid chemisorption reactions by gaseous electrodeless discharges, and have postulated a general mechanism. It was suggested that creation of sites[1-4] can occur by a chain mechanism initiated by the reaction of an active particle G, with a surface atom S, causing a "disso-ciation" of the atom into 2 sites capable of adsorption V. An over-all reaction,

$$G+nS \rightarrow GV+(2n-1)V$$
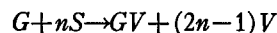
results, yielding $(2n-1)$ sites capable of further adsorption or of suffering bimolecular decay.[2]

If the mechanism is considered to be plausible, and the data of the enhancement effect and the generality of it would seem to indicate this,[1] then a logical and necessary extension of this mechanism leads to the postulate that the energizing of the gaseous reactants of a heterogeneously catalized reaction should lead, in some cases at least, to an enhanced rate of reaction. On this basis it may be predicted that, if H_2 adsorption is prerequisite for hydrogenation on Pd, then the hydrogenation action of that catalyst should be increased by energizing the gas mixture above the catalyst, because the adsorption of H_2 on alumina-supported Pd has been shown to be capable of enhancement[1] by a minute gaseous discharge.

Such energizing may conceivably be accomplished by means of low- or high-energy electromagnetic or corpuscular radiation, or even by ultrasonics. The nature of the applied energy is relatively unimportant if "activated" particles of at least one of the reactants may be caused to form and to persist in sufficient numbers in the gas phase under the chosen conditions for the above mechanism to be operative. Since that mechanism results in a chain process of surface-site production, the stimulus may be expected to be extremely small in comparison to the enhancement.

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Errata: Raman Spectra, Vibrational Assignments, and Force Constants for BH₃CO and BD₃CO

[J. Chem. Phys. 26, 1131 (1957)]

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THE A_1 symmetry coordinates in the above paper formed from the valence angles around the boron atom would be of the correct form only if the angles were tetrahedral. Since this is not the case for BH_3CO, the redundancy condition (as expressed by the S_0 symmetry coordinate) should be written as

$$S_0 = (3+3a^2)^{-\frac{1}{2}}$$
$$\times [\Delta\alpha_{12}+\Delta\alpha_{23}+\Delta\alpha_{31}+a(\Delta\beta_1+\Delta\beta_2+\Delta\beta_3)] \equiv 0.$$

The corresponding nonredundant coordinate, S_4, should be

$$S_4 = (3+3a^2)^{-\frac{1}{2}}[\Delta\alpha_{12}+\Delta\alpha_{23}+\Delta\alpha_{31}-a(\Delta\beta_1+\Delta\beta_2+\Delta\beta_3)]$$

where

$$a = -\frac{\sqrt{3}\,\cos\beta}{\cos\dfrac{\alpha}{2}}.$$

Incorporation of these changes in the normal coordinate treatment leads to revised values for certain force constants as listed below. The agreement between calculated and experimental frequencies is unchanged. The author is indebted to Mr. James Scherer for first bringing this point to his attention.

$F_1 = 17.9900$ md/A	$k_T = 17.9900$ md/A
$F_2 = 2.7750$	$k_R = 2.7750$
$F_4 = 0.5230$	$k_\alpha = 0.2125$
$F_{24} = -0.2790$	$k_\beta = 0.2250$
	$k_{\alpha\alpha} = -0.0309$
	$k_{\beta\beta} = 0.0048$
	$k_{\alpha\beta} = k_{\alpha\beta}' = -0.0627$
	$k_{R\alpha} = -0.0670$
	$k_{R\beta} = 0.0836$

Addendum: Theory of Internal Over-All Rotational Interactions. III. Nonrigid Asymmetric Rotors
[J. Chem. Phys. 23, 2236 (1955)]

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BECAUSE of symmetry considerations, the matrix elements $(r|\mathbf{P}_z|r)$ and $(r|\mathbf{P}_z^3|r)$ appearing in the article are equal to zero. Thus all discussions pertaining to the evaluation of these elements, i.e., Appendix III, should be ignored. The following discussion should be added in order to correct the article.

The matrix elements

$$P_2(r',r) = 1/2(I_{zz}/I_{z1}I_z)(r'|\mathbf{P}_z^2|r) \qquad \text{(a)}$$

$$P_1(r',r) = I_{z1}^{-1}(r'|\mathbf{P}_z|r) \qquad \text{(b)}$$

appear in Eq. (17) but only (r,r) terms are retained, an approximation that is valid provided

$$|P_2(r',r)| \ll |W_{r'} - W_r + P_2(r',r') - P_2(r,r)| \qquad \text{(c)}$$

$$|P_1(r',r)| \ll |W_{r'} - W_r + P_2(r',r') - P_2(r,r)|. \qquad \text{(d)}$$

$(r' \neq r)$. In contradiction to the statements in the article, $P_1(r,r) = 0$. Thus in this approximation all matrix elements of $\mathbf{P}_z$ and $\mathbf{P}_z^3$ vanish in all equations in the article, thereby simplifying the results considerably.

If the rotor is nearly symmetric, the separation between "asymmetry doublets" becomes small, and condition (d) no longer holds. In this event degenerate perturbation theory must be applied. The wave equation described in Eq. (13) should be altered by substituting $2^{-\frac{1}{2}}[\Phi_{r0} \pm \Phi_{r1}]$ in place of Φ_r, where $(r0)$ and $(r1)$ represent the rigid rotor quantum numbers corresponding to the $\gamma = 0$ and $\gamma = 1$ members,[1] respectively, of an "asymmetry doublet." Thus if the inequality in relation (d) is reversed, the equations throughout the article must be altered in the following ways: $W_R(r)$, $(r|\mathbf{P}_z^2|r)$, and $(r|\mathbf{P}_z^4|r)$ should all be replaced by the average of the corresponding $(r0)$ and $(r1)$ values; $(r|\mathbf{P}_z|r)$ should be replaced by $\pm(r0|\mathbf{P}_z|r1)$ where the $(+)$ and $(-)$ refer to the two different states corresponding to the same limiting quantum number K; $(r|\mathbf{P}_z^3|r)$ should be treated analogously to $(r|\mathbf{P}_z|r)$. For a symmetric top, this procedure leads to Eq. (43), except that $\pm K$ should be substituted for K.

The author is greatly indebted to Mr. Dudley Herschbach for his criticisms of Appendix III which led to the present revisions.

[1] King, Hainer, and Cross, J. Chem. Phys. 11, 27 (1943).

Errata: Theory of the Interaction of Internal Rotation with Over-All Rotations. I. Symmetric Rotors: Methyl Silane
[J. Chem. Phys. 22, 1733 (1954)]

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IN the abstract, and in Eqs. (14) and (16), K should be replaced by $\pm K$. See the preceding errata for a discussion of this procedure.

Erratum: Statistical Mechanics of Liquid-Vapor Equilibrium
[J. Chem. Phys. 26, 887 (1957)]

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THIS article should contain a reference to the earlier work of S. Katsura and H. Fujita [Progr. Theoret. Phys. Japan 5, 997 (1950)], to which it is quite closely related, and in which some of the methods of the present paper were anticipated.