

The Calculation of Bond Strengths from Photochemical Evidence

Milton Burton

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to zero as they enter, or it might conceivably be due to a constant defect in the calorimetric method of measuring the hydrogen atom concentration.

In a very careful and exhaustive paper by Poole¹¹ on the general subject of hydrogen atoms, B.S.V.R. Rao points out that Bichowsky and Copeland¹² were in error in their direct determination of the heat of dissociation of the H_2 molecule. In that case there is no longer a direct proof of the correctness of the calorimetric method for estimating hydrogen atom concentrations. It may be pointed out, however, that the agreement between the results of the present paper and the general conclusions of Polanyi,¹ in which the ortho- and parahydrogen conversion

was used as a measure of the hydrogen atom concentration, indicates that the calorimetric method is sound. It seems inconceivable that the reaction of hydrogen atoms with CCl_4 should reach the same limit, namely, 100 percent conversion of the hydrogen atoms into HCl in the range $150-200^\circ$, as a result of counter-balancing errors.

The previous discussion of the reaction rate and its calculation may obscure the fact that at intermediate CCl_4 concentrations, the absolute value of n_{HCl} is essentially determined by the absolute value of n_H . In other words, the reaction may be used to determine the concentration of hydrogen atoms actually entering into a reaction with good accuracy and little difficulty. The conditions necessary for apparatus of this design are: a pressure of approximately 0.8 mm, a temperature of $150-200^\circ$ and a $CCl_4 : H$ ratio of about 10 : 1.

¹¹ H. G. Poole, Proc. Roy. Soc. (London), **163**, 404 (1937).

¹² F. R. Bichowsky and L. C. Copeland, J. Am. Chem. Soc. **50**, 1315 (1928).

The Calculation of Bond Strengths from Photochemical Evidence

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When predissociation manifests itself in polyatomic molecules by a sudden broadening of the rotation lines of a discrete absorption spectrum, a close correspondence is to be expected between the beginning of the predissociation region and the strength of the bond involved. This principle is used to calculate the bond strengths of C—C in ethane, acetaldehyde, acetone and free acetyl (values: 72.1, 93.1, 96.5 and -19.4 kcal., respectively) and of C—H in methane,

O

acetaldehyde ($CH_3C=O$), formaldehyde and free formyl (values: 94.8, 114.7, 103.3, and 0.1 kcal., respectively), where the bond strength is defined in reference to the state of the molecule at $0^\circ K$. Assuming the validity of the method, the bond strength values given are shown to be accurate within 1.0 kcal. The limitations of the method as well as some implications of the results are indicated.

IT is frequently observed in the absorption spectra of diatomic molecules that within the vibrational bands a sudden blurring occurs because of broadening of the rotational lines as the wave-length is decreased. It has been shown that when predissociation is of this kind in polyatomic

molecules a close correspondence may be expected between the beginning of the diffuse region and the strength of the bond ruptured in the attendant photochemical process.² This type of spectrum appears to be present in the cases of formaldehyde, acetaldehyde and acetone. It is proposed in this paper to make the assumption

¹ This paper was begun when the writer was a visitor at the University of California and completed at New York University, which is his present address.

² Cf. Burton and Rollefson, J. Chem. Phys. **6**, 416 (1938).

that correspondence between the threshold of predissociation and the bond strength is exact in these cases and to deduce therefrom the strength of the C-H and C-C bonds in several other compounds and free radicals. The photochemical data alone, of course, are insufficient for this purpose. Such data must be supplemented by the various thermochemical values already available.

DEFINITION OF BOND STRENGTH

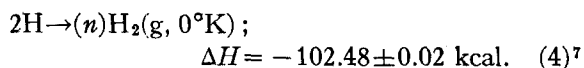
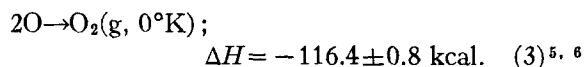
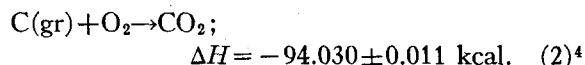
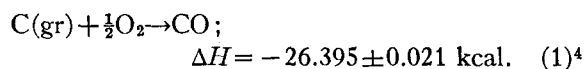
The strength of a bond in a particular compound may be defined as the energy difference (per mole) between the lowest energy state of that compound and the (summed) lowest energy state of the products formed by rupture of that bond. It is essential in giving the bond strength to indicate the products. If, for example, we consider the free acetyl radical, CH_3CO , decomposing into CH_3 and normal CO we find a negative bond strength although a positive heat of activation is required for the process of rupture. On the other hand, if we consider the *immediate* products to be CH_3 and CO in the latter of which there are two unpaired electrons, the bond strength comes out to be positive. In ordinary stable compounds the bond strength will very frequently come out to be the same as the energy required to rupture a bond (the energy of activation for the rupture process) but this equality is not required by the definition. It is evident that the bond strength cannot exceed the energy of activation from the lowest state.

Since the bond strength is defined in reference to the lowest energy states it is necessary that the calculation be conducted in reference to the states of the original compound and of the product atoms or free radicals at 0°K , i.e., for particles devoid of translation and in the lowest vibrational and rotational states.

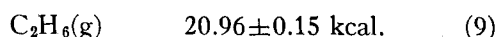
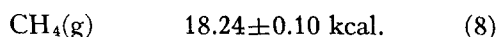
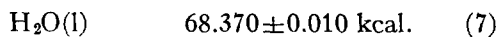
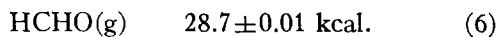
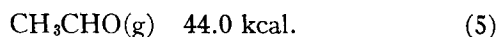
The predissociation process, already referred to, at its threshold is assumed to yield radicals in their lowest rotational and vibrational energy states. It will appear that no correction need be applied to the predissociation data in such compounds to allow for the contribution of energy from available degrees of freedom in the molecule at normal temperatures.

FUNDAMENTAL DATA

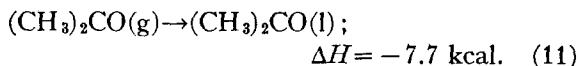
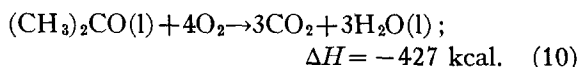
In the estimation of these bond strengths the reliability of the following thermochemical data has been assumed.³



The following heats of formation of substances from their elements in their standard states are given by Bichowsky and Rossini.⁸



The following values are obtained from the *International Critical Tables*.



It has already been mentioned that bond strengths are properly defined in relationship to the molecules at 0°K . To perform the calculations the following data were assumed. The basis on which they were calculated is discussed immediately below.

³ Unless otherwise indicated all chemically stable compounds and carbon, C(gr), are to be presumed to be in their standard states. Radicals and atoms are to be presumed to be in the states corresponding to 0°K .

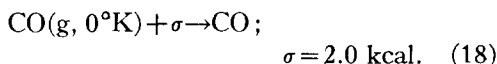
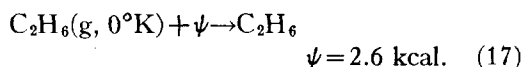
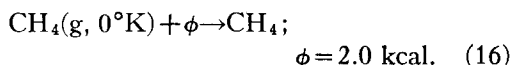
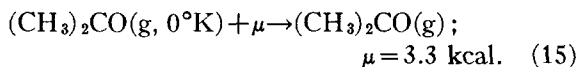
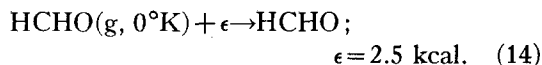
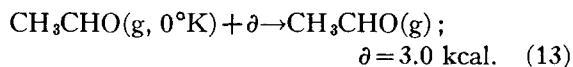
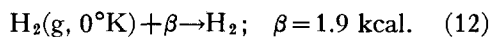
⁴ Rossini, J. Chem. Phys. **6**, 569 (1938).

⁵ Knauss and Ballard, Phys. Rev. **48**, 796 (1935).

⁶ Herzberg, Chem. Rev. **20**, 145 (1937).

⁷ Beutler, Zeits. f. physik. Chemie **B29**, 315 (1935).

⁸ Bichowsky and Rossini, *The Thermochemistry of the Chemical Substances* (Reinhold Publishing Corp., New York, 1936).



Hydrogen.—Giauque's figures⁹ yield 528.1 cal. as the vibrational and rotational energy of $(n)\text{H}_2$ at 291.1°K. To this is added $3RT/2$ for translational energy plus RT for the pressure volume term.

Methane.—The specific heat of methane gas is given by Millar,¹⁰ over the range 142–278°K. Straight-line extrapolation on the high side yields a value for $C_p = 8.37$ cal./mole/deg. at 291.1°K. At 142°K, $C_p = 7.2$. The assumption was made in the calculation that the specific heat from there down fell off linearly to $C_p = 5.0$ at 0°K. The heat content of CH_4 at 291.1°K relative to the gas at 0°K was then calculated from $\int C_p dT$. Such a method of extrapolation is, of course, extremely rough and subject to theoretical criticism. The defense of the method is simply that the error so introduced is small, probably not exceeding 0.2 kcal.

Ethane.—Kemp and Pitzer give a theoretical curve for the specific heat of ethane extending from ~140°K to high temperatures.¹¹ As in the case of methane, it is here assumed that C_p equals 5.0 at 0°K and increases linearly to 140°K. The values used for 140°K and 291.1°K were 9.2 and 12.25 cal./mole/deg. respectively.

Carbon monoxide.—Specific heats are available over the range 83°K to 300°K.¹² They range from 7.27 at the lower temperature to 7.01 cal./mole/

deg. at 291.1°K. As before, the rough assumption (adequate for the present purpose) was made that at 0°K, $C_p = 5.0$, rising linearly to 7.27 at the lower limit of measurement at 83°K.

Acetaldehyde.—Very limited data are available for this compound.¹³ C_p/C_v is given as 1.14 at 30°. From this information a value of $C_p = 16.3$ cal./mole/deg. at 30°C was calculated. The very rough assumption was then made that C_p fell linearly to 5.0 at 0°K and the heat content of gaseous CH_3CHO at 291.1°K relative to the gas at 0°K was calculated on this basis.

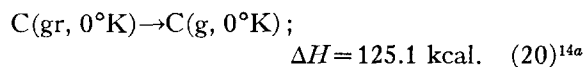
Acetone.—The only specific heat data available for this compound are for greater than normal room temperatures.¹⁴ From these data a value of $C_p = 17.8$ cal./mole/deg. at 291.1°K was calculated on the assumption that the specific heat fell off linearly to 5.0 at 0°K. This is undoubtedly the least justifiable of the approximations so far made. Again the excuse is that the error is not too large; in this case the resultant relative heat content value is probably not more than ~0.5 kcal. too low.

Formaldehyde.—No data at all are available for this compound. The value of ϵ was simply guessed at by comparison of methane with ethane and of acetaldehyde with acetone.

The following data are not essential to the calculation of bond strengths but are included for the purpose of reference so that those who may be interested in the heats of formation of compounds and radicals from their gaseous atoms may find such information here. In such calculations it is necessary to know the heat of sublimation of graphite and, in turn, the heat of formation of CO from the gaseous atoms. The values favored by Herzberg⁶ (and which are by no means uncontested) are



and the consequent



¹³ *International Critical Tables*. Wüllner, Ann. d. Physik **4**, 321 (1878).

¹⁴ *International Critical Tables*; Regnault, Ann. chim. phys. **24**, 342 (1871).

^{14a} The value of 124.1 kcal. actually given by Herzberg depends on an earlier value for ΔH in reaction 1 than that given here.

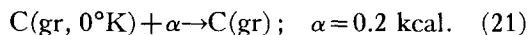
⁹ Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

¹⁰ Millar, J. Am. Chem. Soc. **45**, 874 (1923).

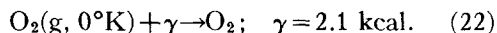
¹¹ Kemp and Pitzer, J. Am. Chem. Soc. **59**, 276 (1937).

¹² *International Critical Tables*; Scheel and Heuse, Ann. d. Physik **40**, 473 (1913).

The value for the reaction



is obtained from Nernst.¹⁵ The value for



is obtained by a calculation similar to that used for carbon monoxide.¹²

CALCULATIONS

The above data have been used to calculate the heats of formation of various gaseous substances from their *atomic* elements. These values are assembled in Table I together with an indication (in the column labeled "Source of Data") of the method of calculation. The heats of formation given in the column headed C(gr, 0°K) are based on graphite as the reference state for carbon; those given in the column headed C(g, 0°K) are based upon the assumptions of Herzberg already noted. The nature of the approximations is clearly indicated in both cases. As to the relative accuracy of the two sets of data, the former are probably correct within 1.0 kcal. Although the latter may be just as accurate, it is not likely that they will be accepted without opposition by all the workers interested in this field.

For further calculations it is now necessary to use our knowledge of the predissociation limits of CH₃CHO, HCHO and (CH₃)₂CO. The discrete absorption spectrum of acetaldehyde extends to

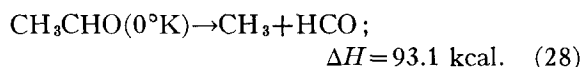
TABLE I. Heats of formation of several gaseous substances at 0°K from their atoms.^a

SUBSTANCE	HEAT, KCAL. PER MOLE		SOURCE OF DATA	REF.
	C(gr, 0°K)	C(g, 0°K)		
CH ₃ CHO	307.2-2α-2β-(γ/2)+θ =305.0	557.4+Σ ²³ =555.2	3, 4, 5; 12, 13 21, 22; 20	23
HCHO	189.4-α-β-(γ/2)+ε =188.8	314.5+Σ ²⁴ =313.9	3, 4, 6; 12, 14 21, 22; 20	24
CH ₄	223.2-α-2β+φ =221.2	348.3+Σ ²⁵ =346.3	4, 8; 12, 16 21; 20	25
C ₂ H ₆	328.4-2α-3β+ψ =325.1	578.6+Σ ²⁶ =575.3	4, 9; 12, 17 21; 20	26
(CH ₃) ₂ CO	418.1-3α-3β-(γ/2)+μ =414.1	793.4+Σ ²⁷ =789.4	2, 3, 4, 7, 10 11; 12, 13; 21, 22; 20	27

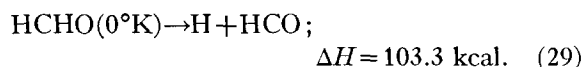
^a The Σ term in the column headed C(g, 0°K) is the sum of the Greek letter terms in the column headed C(gr, 0°K).

¹⁵ *International Critical Tables*; Nernst, Ann. d. Physik **36**, 395 (1911).

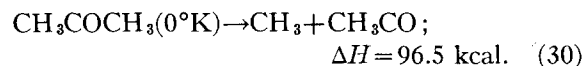
λ3050Å¹⁶ at which wave-length corresponding to 93.1 kcal. per mole, the diffuse spectrum begins. This value can be taken as the strength of C-C bond in CH₃CHO.² There is indirect evidence for slight free radical production¹⁷ at wave-lengths of 3130Å and less but this can be attributed² to the contribution from available vibrational degrees of freedom of the acetaldehyde molecule.¹⁸ It is a reasonable assumption that the time required for the transfer of such energy is so long as to yield a discrete absorption spectrum and that the predissociation limit would be practically the same in a molecule devoid of vibrational or rotational energy. We therefore write



Similarly the sharp line absorption spectrum of formaldehyde becomes diffuse at λ2750Å¹⁹ (≈103.3 kcal.). There is fairly good evidence^{2, 20} that the light absorbed in the diffuse region results in the formation of free hydrogen atoms. We therefore write



In acetone, discrete absorption fades out at λ2945Å²¹ (≈96.5 kcal.). The evidence²² indicates that the decomposition in the diffuse region is exclusively via a free radical mechanism, whereas in the discrete region ultimate molecules are formed in the primary act. We write



The heats of formation of some free radicals shown in Table II are calculated from these three equations and from the data given in Table I. As before, the method of calculation is indicated in the column titled "Source of Data."

¹⁶ Schou, J. Chem. Phys. **27**, 27 (1929); Leighton, Chem. Rev. **17**, 393 (1935).

¹⁷ Blacet and Roof, J. Am. Chem. Soc. **58**, 278 (1936). Cf. Rollefson, J. Phys. Chem. **41**, 259 (1937), Burton, ibid. **41**, 322 (1937).

¹⁸ Cf. Franck and Herzfeld, J. Phys. Chem. **41**, 97 (1937). ¹⁹ Henri and Schou, Zeits. f. Physik **49**, 774 (1929).

²⁰ Patat, Zeits. f. physik. Chemie **B25**, 208 (1934); Löcker and Patat, ibid. **B27**, 431 (1934).

²¹ Noyes, Duncan and Manning, J. Chem. Phys. **2**, 717 (1934).

²² Spence and Wild, J. Chem. Soc. 352 (1937).

It is now possible to calculate several bond strengths from the data thus far given. The results of such calculation are assembled in Table III. Assuming the validity of the method, and taking into account the fact that the errors in the approximations (the Greek-letter terms) cancel each other to a large extent, it follows that the bond strengths given are accurate within 1 kcal.

DISCUSSION

Significance of the bond strength values

In one sense there is nothing new in the ideas suggested by Table III. We are already accustomed to the notion that there is some difference in the strength of a particular bond in different types of compounds.²³ On the other hand, it is not usual to have in one table a listing for the C—C bond ranging from -19.4 kcal. (for CH_3CO) to 96.5 kcal. (for CH_3COCH_3). However, these two values are not really as far apart as they seem. The CO formed in the decomposition of CH_3CO ³⁷ does not have the same electron configuration as the CO in the CH_3CO radical. In fact, it seems that approximately 100 kcal. are liberated in the conversion of CO from a free radical (with two unpaired electrons) to a stable molecule (with all electrons paired).²⁴ The potential energy relationships involved are shown in Fig. 1. Curve *a* represents the normal repulsive curve between a methyl radical and an unactivated carbon monoxide molecule. At values of *r* approaching infinity the potential energy of this system is ~ 100 kcal. less than that of the methyl plus activated carbon monoxide (CO^*) system. Thus, the strength of the C—C bond in the CH_3CO relative to $\text{CH}_3 + \text{CO}^*$, is $\sim 100 - 19.4$

TABLE II. *Heats of formation of some free radicals from their atoms.*

SUBSTANCE	HEAT, KCAL./MOLE		SOURCE OF DATA	REF.
	C(g, 0°K)	C(g, 0°K)		
HCO	$86.1 - \alpha - \beta - (\gamma/2) + \epsilon = 85.5$	$211.2 + \Sigma = 210.7$	24, 29	31
CH_3	$128.0 - \alpha - \beta + \theta - \epsilon = 126.3$	$253.1 + \Sigma = 251.4$	23, 28, 31	32
CH_3CO	$193.7 - 2\alpha - 2\beta - (\gamma/2) + \mu - \theta + \epsilon = 191.0$	$443.9 + \Sigma = 441.2$	27, 30, 32	33

²³ Cf. Kistiakowsky, J. Phys. Chem. **41**, 175 (1937).

²⁴ Cf. Norrish, Trans. Faraday Soc. **30**, 103 (1934).

TABLE III. *Bond strengths.*

BOND	COMPOUND OR FREE RADICAL	STRENGTH, KCAL./MOLE	SOURCE OF DATA	REF.
C—C	C_2H_6	$72.4 - \beta + \psi - 2\theta + 2\epsilon = 72.1$	26, 32	34
	CH_3CHO	93.1	28	35
	CH_3COCH_3	96.5	30	36
	CH_3CO	$-18.2 - \beta - \sigma + \mu - \theta + \epsilon = -19.4$	1, 32, 33	37
C—H	CH_4	$95.2 - \beta + \phi - \theta + \epsilon = 94.8$	25, 32	38
	$\text{CH}_3\text{C}\equiv\text{O}$	$114.5 + 2\theta - \mu - \epsilon = 114.7$	23, 33	39
	HCHO	103.3	29	40
	HCO	$1.5 - \beta - \sigma + \epsilon = 0.1$	1, 31	41

or ~ 80.6 kcal., a value more consistent with its strength in such compounds as ethane.

An estimate as to the value of *A* in Fig. 1 may be gleaned from the fact^{22, 25} that although CH_3CO is stable at room temperatures it is apparently completely unstable above 60° . If we assume that the rate of the decomposition $\text{CH}_3\text{CO} \rightarrow \text{CH}_3 + \text{CO}$ is 10^6 to 10^{12} times greater at 60° than at 0° , it appears that the energy of activation of the decomposition (i.e., *A*) is 4.2 to 8.4 kcal., which may be compared with Rice and Herzfeld's estimate²⁶ of ~ 10 kcal.

The potential energy relationships for HCO are similar to those for CH_3CO . However, the strength of the H—C bond (relative to $\text{H} + \text{CO}^*$) is much greater than that of the C—C bond (relative to $\text{CH}_3 + \text{CO}^*$). The value of *A* in this case, estimated from the great stability of HCO,²⁷ appears to be rather large. On the other hand, the readiness with which H and CO combine,²⁸ indicates that $A - 0.1$ kcal. may not be very great. It is possible, however, to arrive at a false estimate from these latter data, for the combination reaction is probably a three-body process.

JUSTIFICATION OF BOND STRENGTH VALUES

The values of 72.1 kcal. for the bond strength of C—C in ethane and of 94.8 kcal. for C—H in methane are quite in line with those generally accepted at the present time.¹⁴ They are to be compared with the values of 72–76 and ~ 95 kcal., respectively, employed by Rice and Herzfeld in their calculation of the chain decomposition of

²⁵ Glazebrook and Pearson, J. Chem. Soc. 567 (1937).

²⁶ Rice and Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934).

²⁷ Cf. Burton, J. Am. Chem. Soc. **58**, 1655 (1936); J. Phys. Chem. **41**, 322 (1937); J. Am. Chem. Soc. **60**, 212 (1938).

²⁸ Cf. Frankenburger and co-workers, Zeits. f. Elektrochem. **36**, 757 (1930).

ethane. It is interesting that the method of calculation employed in this paper involves the assumption of three values, for C—C in acetaldehyde (35) and acetone (36) and for C—H in formaldehyde (40), which might be subject to criticism. Their best justification is that they are consistent with the C—C value in C_2H_6 and with the C—H value in CH_4 .

The values for C—C in acetaldehyde and acetone disagree with those determined by Rice and Johnston²⁹ from mirror experiments at $\sim 1100^\circ K$. Their values are 69.4 and 70.9 kcal., respectively. It is possible that similar experiments conducted at lower temperatures might yield information as to the cause of the disagreement with the values here quoted. Nevertheless, it is interesting to see under what conditions their values may be made to fit the values of 72.1 kcal. for C—C in ethane and 94.8 kcal. for C—H in methane. Simple calculation shows that a value of ~ 80 kcal. for the C—H bond in formaldehyde is all that is necessary. However, it is apparent that this is an extraordinarily low value for the strength of the C—H bond in a stable compound, particularly in view of the assumed strength of the C—C bond in acetaldehyde. Patat and Sachsse,³⁰ for example, have assumed the much higher value of 92 kcal.

One interesting result of the view of the bond strengths in $HCHO$, CH_3CHO and CH_3COCH_3 presented in this paper is that it would entail a much lower steady-state concentration of free atoms and radicals in the pyrolyses of those compounds. This result would be consonant with the findings of Patat and Sachsse, who used the

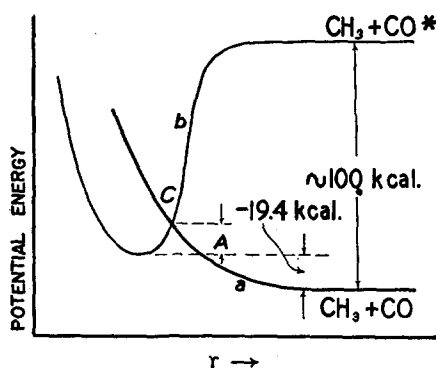


FIG. 1.

para-ortho hydrogen conversion method for the counting of free radicals in the steady state.³⁰

Limitations of the method

This method of calculating bond strengths can only be used in those cases in polyatomic molecules where the predissociation process manifests itself in a sudden broadening of the rotation lines in a clearly defined portion of the spectrum. Furthermore, it is essential to know the chemical process involved. Thus, in the case of benzene, predissociation is observed but we are not informed as to the process involved (there is no net yield of products) and the spectrum itself³¹ is not suitable to our purpose.

In the case of benzaldehyde, although the products of the photolysis are well known the diffuse spectrum appears sharply at $\lambda 2428A$ after a transparent region extending from 2599 to 2428A.³² This type of spectrum is unsuited for these calculations.

²⁹ F. O. Rice and W. R. Johnston, J. Am. Chem. Soc. **56**, 214 (1934).

³⁰ Patat and Sachsse, Zeits. f. physik. Chemie **B31**, 105 (1935).

³¹ Cf. Henri, J. de phys. et rad. (6) **3**, 181 (1922).

³² Henri, *The Structure of Molecules*, P. Debye, Editor (Blackie and Son, Ltd. London, 1932), p. 124.