where W_m is a weighting factor which depends on the particle size. W_m is proportional to the number of particles, N_m, of a given size, to the intensity, I_m, diffracted by a single particle of a given size, and inversely proportional to the area, A_m, of the diffraction function for particles of a given size. I_m is very nearly proportional to the volume of the crystal. It can be seen from the Scherrer equation and the theoretical diffraction functions that A_m is inversely proportional to the cube root of the volume of the crystals. Then the weighting factor is $W_m = CN_mV_m^{4/3}$. The resultant diffraction function due to a mixture of sizes will then be

$$F(y) = \sum_m N_mV_m^{4/3}F(a_my)/\sum_m N_mV_m^{4/3}.$$

The half-maximum intensity breadth of this function will give the observed mean size of the particles. Since the diffraction function is weighted in favor of the larger particles, the measured mean size will be expected to be too large in practice. The effect on the diffraction function of various distributions of particle size was investigated using the above relation. A discrete distribution of particle sizes, approximating the continuous Gaussian distribution, does not seem to change the shape of the diffraction function appreciably. However, a distribution in which there are a large number of relatively small particles gives a diffraction function which is broad near the base. For example, the calculation was made for the 220 reflection from cube-shaped particles when there are four times as many particles of 75 angstrom edge length as of 150 angstrom edge length. The half-intensity breadth gave a mean edge length of 135 angstrom units, but the resultant line shape corresponded to the shape for cubes of uniform size only in the upper half. In the lower half the resultant function was much broader than the function for cubes of uniform size. It seems reasonable that some such distribution of particle sizes may account for the experimentally determined diffraction functions.

The author wishes to thank Professor Carleton C. Murdock, who suggested the problem, for his encouragement and assistance in carrying out the research.

PHYSICAL REVIEW VOLUME 72, NUMBER 10 NOVEMBER 15, 1947

On the Dissociation Energy of Carbon Monoxide and the Heat of Sublimation of Carbon

Homer D. Hagstrum
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received June 26, 1947)

None of the values of the dissociation energy of carbon monoxide, D(CO), proposed on the basis of interpretations of predissociations in the spectrum of CO is in satisfactory agreement with the results of electron-impact experiments. The only possible interpretation of these experiments gives $D(\mathrm{CO}) = 9.6$ ev. Compelling reasons can be given for considering this result of sufficient accuracy to make it irreconcilable with any of the values from the band spectrum. A new interpretation of the effects in the spectrum which brings agreement with the electron impact value is possible, however. It involves a potential curve with maximum for $J=0$ for the state $a'\,{}^3\Sigma^+$ of CO which predissociates $B^1\Sigma^+$ and $b^3\Sigma^+$ at 11.11 ev. Various data favor this interpretation and its consequences. Satisfactory agreement among all data bearing on D(CO) and L_1(C), the heat of sublimation of carbon, can be attained in this way.

1. INTRODUCTION

THE dissociation energy of carbon monoxide, D(CO), is a particularly important quantity because of its relation to the heat of sublimation of carbon, L_1(C), and through it to the heats of formation and bond energies of every carbon-containing molecule. The relation between L_1(C) and D(CO) is obtained from the well-known thermochemical cycle:

$$\begin{aligned} CO(X^1\Sigma^+)+D(CO) &= C(^3P)+O(^3P)\\ C(^3P) &= C_{\text{solid}}+L_1(C)\\ O(^3P) &= \tfrac{1}{2}O_2(X^3\Sigma_g^-)+\tfrac{1}{2}D(O_2)\\ C_{\text{solid}}+\tfrac{1}{2}O_2(X^3\Sigma_g^-) &= CO(X^1\Sigma^+)+Q(CO)\\ \hline D(CO) &= L_1(C)+\tfrac{1}{2}D(O_2)+Q(CO). \end{aligned}$$

With the well-established values:

$$D(O_2)=5.082 \text{ ev } (117.2 \text{ kcal})^{1,2}$$
$$Q(CO)=1.180 \text{ ev } (27.20 \text{ kcal})^{3}$$

there is obtained:

$$L_1(C)=D(CO)-3.721 \text{ ev } (85.78 \text{ kcal}).$$

General agreement concerning the value of $D(CO)$ has not yet been reached. The most widely accepted value is that proposed by Herzberg,[4] $D(CO)=9.14$ ev, based on an interpretation of the evidences of predissociation in the spectrum of CO. However, it is one of three divergent values, based on as many interpretations of intensity breakoffs in the band spectrum, currently supported in the literature. Furthermore, one cannot reconcile the electron-impact value, $D(CO)=9.6$ ev, with any of the values from the band spectrum without assuming an error of about 0.5 ev or more. The main purpose of this paper is to discuss critically the data from electron impact and the band spectrum and to propose a new interpretation of the evidences of predissociation in the spectrum which brings agreement with $D(CO)=9.6$ ev.[5] Other data bearing on $D(CO)$ and $L_1(C)$ are discussed and shown to be in harmony with the contention that $D(CO)=9.6$ ev.

2. ELECTRON-IMPACT EXPERIMENTS

Criticism of Method

A review of the literature on electron-impact experiments indicates a considerable lack of agreement among the results obtained by several different methods for a number of molecules. This is no doubt the reason for the evident lack of confidence in the results for CO and the feeling that, in general, the electron impact results give at most upper limits for the quantities measured. Such need not necessarily be true of all the electron impact results, however. A criticism of the methods used and a conclusion as to which may be expected to yield credible results is demanded.

The electron-impact apparatus which have been used in the study of ionization and dissociation processes in CO are these: (a) a Lenard-type apparatus with positive-ray analysis of the ions produced;[6] (b) an apparatus which detects the ions formed as well as the variation of the electron current passing through the gas as a function of electron energy;[7] (c) a mass spectrometer having a "transverse," magnetically-collimated electron beam;[8–10] and (d) a retarding potential apparatus used to study ions which receive appreciable initial kinetic energies in their formation.[11,12]

The first of these apparatus belongs to a general type used by several investigators with which was obtained no general agreement or convincing evidence concerning the ionization *and dissociation* of molecules at a single electron collision. The gas pressures employed were high enough to cause secondary processes to occur. For some molecules, in fact, it could not be decided whether the atomic ions observed resulted from a primary process involving ionization and dissociation of the molecule or a second-

---

[1] G. Herzberg, *Molecular Spectra and Molecular Structure, I. Diatomic Molecules* (Prentice Hall, New York, 1939), pp. 474ff.

[2] In this paper, the conversion factors: 1 ev $=8066.0$ cm^{-1} $=23.053$ kcal/mole are used. See Table II, G. Herzberg, reference 1. Values in the literature based on other conversion factors have been recalculated for quotation in this paper.

[3] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, J. Research Nat. Bur. of Stand. Wash. **34**, 143 (1945).

[4] G. Herzberg, Chem. Rev. **20**, 145 (1937).

[5] The gist of this interpretation has been published as a preliminary report in a Letter to the Editor of this journal, H. D. Hagstrum, Phys. Rev. **71**, 376 (1947) and was discussed at the Washington meeting of the American Physical Society, May 1, 1947, H. D. Hagstrum, Phys. Rev. **72**, 158 (1947).

[6] T. R. Hogness and R. W. Harkness, Phys. Rev. **32**, 936 (1928).

[7] J. Savard, Rev. Fac. Sci. Univ. Istanbul **II**, 235 (1937); M. de Hemptinne, J. Savard, and P. Capron, Compt. Rend. Acad. Sci. Paris **204**, 1039 (1937); J. Savard and M. de Hemptinne, J. de phys. et rad. **10**, 30 (1939). See also the report of the work on N_2: M. de Hemptinne and J. Savard, J. de phys. et rad. **6**, 499 (1935).

[8] A. L. Vaughan, Phys. Rev. **38**, 1687 (1931).

[9] J. T. Tate, P. T. Smith, and A. L. Vaughan, Phys. Rev. **48**, 525 (1935).

[10] H. D. Hagstrum and J. T. Tate, Phys. Rev. **59**, 354 (1941).

[11] J. T. Tate and W. W. Lozier, Phys. Rev. **39**, 254 (1932).

[12] W. W. Lozier, Phys. Rev. **46**, 268 (1934).

ary process in which a molecular ion (the result of a primary electron-impact process) is dissociated on collision with another molecule. Furthermore, the sensitivity of the apparatus was generally considerably lower than that attained in later work. Thus Hogness and Harkness,[6] although they thought that the O^+ ion resulted from the primary process $CO+\epsilon^- \rightarrow C+O^+ +2\epsilon^-$, could not measure its appearance potential and had difficulty in distinguishing $CO+\epsilon^- \rightarrow C^+ +O+2\epsilon^-$ from $CO^+ +CO \rightarrow C^+ +CO_2$. For these reasons it is believed that appearance potentials obtained by this method as well as their interpretation, may be unreliable and should not be used to calculate dissociation energies.

About 1930 there were constructed apparatus in which the ions are formed in a magnetically-collimated electron beam of restricted cross section [methods (c) and (d)].[13] Greater sensitivity was attained and care taken to avoid the occurrence of secondary processes in the ionization chamber. This marked a definite turning point in the study of ionization and dissociation processes in molecules by electron impact.

The method employed by Savard and de Hemptinne,[7] listed as (b) above, is for several reasons considered to be unreliable and to yield questionable results. The ions produced in the apparatus were not identified by (m/e)-analysis nor distinguished on the basis of their initial kinetic energy. No positive means of attributing the breaks in the collector-current curve to the onset of particular ionization processes was available. Some processes were attributed to the collision of an electron with an ion formed in an earlier collision. The occurrence of these processes can only mean that the gas pressure used, although not specified, was sufficiently high to cause other secondary processes to occur and thus to make questionable any of the results claimed. On the basis of the appearance of what were thought to be C^+ ions at 20.0 ev, the authors maintain that $D(CO)=8.8$ ev.[7] However, similar measurements in N_2 yielded $D(N_2)=6.72$ ev[7] in disagreement with the value $D(N_2)=7.384$ ev now generally accepted.[14]

Other aspects of the experiment of Savard and de Hemptinne confirm one's doubts as to its validity. Ion and electron currents were allowed to mix, leading, as the authors themselves admit, to spurious maxima in the collected current. The observation of some ionization processes was said to depend critically upon the attainment of what was considered to be a balance between the rates of gas inlet into the apparatus and gas removal in the form of ions produced. It was claimed that as many as 58 critical potentials had been found in CO in the electron-energy range 12.5 to 34.0 ev.[15] Some of these potentials depend upon the deviation of a single datum point from the general course of the current curve. This work has been refuted in such detail because it has been injected into the discussion of $D(CO)$ by Long and Norrish[16] alongside other electron-impact results as evidence of discord among such results.

In contrast to the methods (a) and (b) just discussed, methods (c) and (d) are believed now to yield trustworthy results. The reasons for this belief are to be discussed in detail presently. The deficiencies in the work of Vaughan,[8] Tate, Smith, and Vaughan,[9] and Tate and Lozier[11] in CO have been removed in the later work.[10,12] Reference is made to the original literature for discussions of the apparatus and the methods of their use.[17]

Criticism of Data and Interpretation

The value of $D(CO)$ from electron-impact experiments rests on the onset potentials of the following observed ionization and dissociation processes:

$$\begin{aligned}
&(A)\quad CO+\epsilon^- \rightarrow C^+ +O+2\epsilon^-\\
&(B)\quad CO+\epsilon^- \rightarrow C^+ +O^- +\epsilon^-\\
&(C)\quad CO+\epsilon^- \rightarrow C+O^+ +2\epsilon^-\\
&(D)\quad CO+\epsilon^- \rightarrow C+O^-.
\end{aligned}$$

The measured onset potentials of these processes are given in Table I. Typical experimental data

---

[13] W. Bleakney, Phys. Rev. **34**, 157 (1929); **35**, 139 and 1180 (1930); W. W. Lozier, Phys. Rev. **36**, 1285 (1930).

[14] G. Herzberg and H. Spöner, Zeits. f. physik. Chemie **B26**, 1 (1934); reference 1; W. W. Lozier, Phys. Rev. **44**, 575 (1933); **45**, 840 (1934); H. D. Hagstrum and J. T. Tate, Phys. Rev. **59**, 354 (1941).

[15] In this connection see E. Rudberg, Proc. Roy. Soc. London [A]**130**, 182 (1930) in which the energy losses of electrons in passing through CO are measured directly.

[16] L. H. Long and R. G. W. Norrish, Proc. Roy. Soc. London [A]**187**, 337 (1946).

[17] A general description of mass spectrometers is to be found in E. B. Jordan and L. B. Young, J. App. Phys. **13**, 526 (1942). For a discussion of the extension of the mass-spectrometric method [method (c)] to include an analysis of ion-peak shapes see reference 10. The retarding-potential method [method (d)] is described in reference 12.

TABLE I. Onset potentials of ionization and dissociation processes in CO.

		Lozier[12] (ev)	Hagstrum and Tate[10] (ev)
Process (A)	$A(C^+)$	22.8 ± 0.1	22.8 ± 0.2
Process (B)	$A(C^+)$	20.9 ± 0.1	20.9 ± 0.2
	$A(O^-)$	20.9 ± 0.1	20.9 ± 0.2
Process (C)	$A(O^+)$	—	$23.1^{+0.0}_{-0.4}$
Process (D)	$A(O^-)$	9.5 ± 0.1	9.5 ± 0.2

from which they are obtained are reproduced in Figs. 1 and 2.

If these data are to be used to determine dissociation limits of the molecule, it is essential (1) that each process be identified correctly, (2) that its measured onset potential be the appearance potential of ions of zero initial kinetic energy, and (3) that the electron energy at the onset of ionization be correctly determined from the ionization-efficiency curve at its foot.

When a mass spectrometer is employed [method (c)], the nature of one of the dissociation products is evident from the (m/e)-analysis. The retarding-potential apparatus [method (d)], with which no (m/e)-analysis is made, can distinguish positive and negative ions and the ions which, because they result from a dissociation process, possess appreciable initial kinetic energies. At a given retarding potential, the appearance potential of the positive ion formed at the lowest electron energy is measured by this method. This ion may be identified by the mass spectrometer. Thus in CO, the C^+ ion is found in the mass spectrometer to occur at lower electron energies than the O^+ ion, identifying the positive ion studied in Lozier's work. The negative ion is identified as O^- in the mass spectrometer.

From the simultaneous appearance of positive and negative ions or from the magnitude of the onset potential, one can generally determine the state of ionization of the other dissociation product. Thus the appearance of C^+ and O^- at 20.9 ev in equal numbers up to 22.8 ev (see Fig. 1) identifies process (B). Since the value 22.8 ev for the second appearance potential of C^+ ions is less than the sum of the ionization energies of C and O one concludes with confidence that only C^+ ions are formed at 22.8 ev and that process (A) has been identified correctly. Similar arguments apply to processes (C) and (D). Because $A(O^+)>A(C^+)$, process (C) could not be studied by method (d). No evidence of the occurrence of secondary processes is to be found in these experiments.

The identification of the state of excitation of the products cannot be made directly in an electron-impact experiment. From the onset potential of a single process, a series of possible levels for a given dissociation limit may be calculated for various assumed states of excitation of the products. From such results for more than one process, a unique determination is possible in CO as is to be explained.

In the retarding potential method the kinetic energy of the ion as well as its appearance potential is measured. From these data the appearance potential of ions formed at rest may be calculated by the law of conservation of momentum at the collision.[12] This determination is valid even if ions of zero initial kinetic energy are not formed as is the case when the potential curve involved has a maximum. In addition, the analysis of the shapes of ion peaks has demonstrated

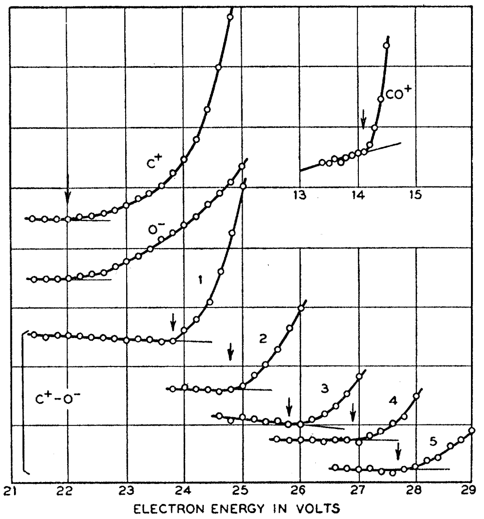

FIG. 1. Typical experimental data of Lozier (Figs. 8 and 9 of reference 12) from which appearance potentials are obtained in the study of CO by method (d). The appearance potential of CO^+ is used to calibrate the voltage scale. The total kinetic energy of the C^+ and O^- ion products is 1 ev. The curves 1 to 5 for the difference current C^+-O^- correspond to total kinetic energies of 1, 2, 3, 4, and 5 ev, respectively. Note the equality of the C^+ and O^- currents to 22.8 ev (for ions of zero initial kinetic energy), the onset potential of the process yielding C^++O. These curves show how difficult it would be to assume an experimental error of greater than ±0.1 ev in these results.

that considerable information concerning the distribution in initial kinetic energy of the ions formed and hence the nature and position of the potential curve involved can be obtained with the mass spectrometer.[10] Study of a single molecule by both methods gives more information than by either method alone. In CO, the appearance potentials of ions of zero initial kinetic energy in processes (A), (B), and (D) determined by the retarding-potential method agree with those for ions at the maximum of the peak observed with mass spectrometer. This, together with the observed peak shape, demonstrates that the ions are formed at rest and that the data may be used to fix dissociation limits of the molecule. The study of process (C) with the mass spectrometer, on the other hand, showed that O^+ ions of zero initial kinetic energy are not formed. This necessitated the use of a special method to obtain the energy level of the corresponding dissociation limit.[10]

In the electron impact experiments of interest here, the lowest electron energy at which an ion is detected is taken as the onset potential of the process of its formation. The voltage scale is calibrated against the ionization of a rare gas, due precautions being taken to adjust to comparable instrumental sensitivity. The appearance potential is the point at which the ionization-efficiency curve first breaks away from the base line in Figs. 1 and 2.

The justification of the whole procedure of these experiments, and of the choice of the onset potentials in particular, is to be found in the results for molecules whose dissociation energies are well established by other means. Studies have been carried out in H_2, N_2, NO, and O_2 with apparatus and procedure identical to that used in CO. In Table II the relevant appearance potentials are listed and the dissociation energies obtained from them compared with the generally accepted values.[18] Further evidence of the reliability of the method is to be found in the values obtained for various ionization potentials known by other means (see Table III).

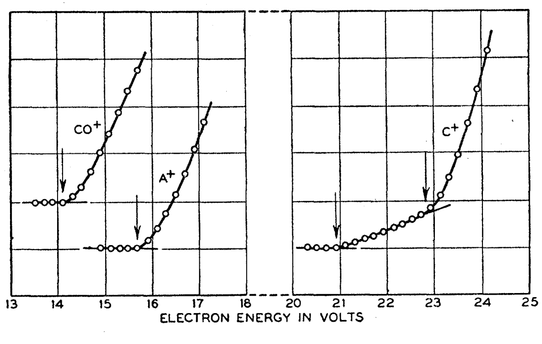

FIG. 2. Typical experimental data of Hagstrum and Tate (Fig. 12 of reference 10) from which appearance potentials are obtained in the study of CO by method (c). The appearance potential of A^+ ions is used to calibrate the voltage scale. The onset of the two processes forming C^+ ions [(*A*) and (*B*)], here of zero initial kinetic energy, are clearly seen. The maximum experimental error is given as ±0.2 ev.

TABLE II. Comparison of dissociation energies from electron impact and other data.

Molecule	Appearance potential (ev)	Dissociation energy (ev) Electron impact	Dissociation energy (ev) Established value
H_2	$A(H^+)=18.0\pm0.2$[19] $=17.96\pm0.03$[20] $=18.0\pm0.2$[10]	4.5[20,10]	4.4776[22]
N_2	$A(N^+)=24.27\pm0.1$[20] $=24.3\pm0.2$[10]	7.4[20,10]	7.384[14,22]
NO	$A(N^+)=21.7\pm0.2$[21] $=21.8\pm0.2$[10]	5.3[21,10]	5.29[22]

In the earlier work of Vaughan[8] with a mass spectrometer and of Tate and Lozier[11] with a retarding-potential apparatus, processes (A) and (B) were not satisfactorily distinguished. This has now been done, as has been discussed, with excellent agreement between the two methods (Table I). Tate, Smith, and Vaughan's value[9] of $A(O^+)$ was measured at the maximum of the O^+ peak which later work[10] showed not to correspond to ions of zero initial kinetic energy.

A consistent interpretation of the onset potentials in Table I is obtained only if $D(CO)=9.6\pm0.1$ ev. The 22.8 ev onset potential of process (A) makes the values $D(CO)=11.6$, 9.6, 7.4, 6.4 and 4.4 ev possible for various choices of excitation of the products. The onset potential of process (C), however, yields a series of values which contains only the value 9.6 ev of those

---

[18] In the case of O_2, Lozier did not study the process $O_2+\epsilon^-\rightarrow O^++O+2\epsilon^-$ (reference 12) and the analysis with the mass spectrometer indicates that the potential curve involved possesses a maximum.[10] No definite statement concerning $D(O_2)$ can be made on the basis of electron-collision experiments alone without the retarding-potential study.

[19] W. Bleakney, Phys. Rev. **35**, 1180 (1930); **40**, 496 (1932).

[20] W. W. Lozier, Phys. Rev. **44**, 575 (1933); **45**, 840 (1934).

[21] E. E. Hanson, Phys. Rev. **51**, 86 (1937).

[22] See reference 1, Tables 36 and 37, pp. 482 and 500.

TABLE III. Comparison of ionization potentials from electron impact and other data. Note: In these cases transitions between the lowest vibrational states of the ground electronic states of the ion and molecule can occur by the Franck-Condon principle.

Ionization potential	Electron impact (ev)	Spectroscopic (ev)
$I(H_2)$	15.4±0.1[19,10]	15.427[22]
$I(N_2)$	15.7±0.1[9,10]	15.581[22]
$I(O_2)$	12.3±0.1[10]	12.2[22]
$I(Ne)-I(A)$	5.65±0.15[23]	5.78

listed. The processes (B) and (D) can be interpreted satisfactorily with $D(CO)=9.6$ ev.[10,12] It should be emphasized that the value of $D(CO)$ rests upon $A(C^+)=22.8\pm0.1$ ev from both electron-impact methods. $A(O^+)$ is not as accurate as $A(C^+)$ and is used only to discriminate among the values of $D(CO)$ listed above.

A schematic diagram of the energy levels at which the various ionization and dissociation processes commence and the assignment of dissociation limits of CO, CO^+, and CO^- is shown in Fig. 3. Included in the figure are the assignments based on three values of $D(CO)$ proposed on the basis of band spectroscopic evidence. These are to be discussed in detail later. Note that only the dissociation limits based on $D(CO)=9.6$ ev can account for the observed processes. It is difficult to see the justification for the remark of Gaydon and Penney[24] that this result is obtained from a curve which "appears to be of complex structure and might be capable of an alternative explanation." $D(CO)=9.6\pm0.1$ ev gives $L_1(C)=5.9\pm0.1$ ev $=136\pm2$ kcal.

3. PRESENT INTERPRETATIONS OF THE SPECTROSCOPIC EVIDENCE

Inasmuch as no band convergence has been found in the spectrum of CO and little if any evidence is to be obtained from absorption continua, one must rely on predissociation data in attempting to fix dissociation limits of the molecule by spectroscopic means. The Birge-Sponer extrapolation of vibrational levels in the ground state yields the value $D(CO)=11.34$ ev,[25] but, as pointed out by Herzberg,[26] this may be as much as 20 to 40 percent too high. This conclusion is in agreement with Gaydon's summary of results of the use of the Birge-Sponer extrapolation for neutral molecules with nonionic binding.[27] Gaydon finds that the average ratio of the known dissociation energy to the value found by linear extrapolation of the vibrational levels for a number of such molecules is 0.79.

Evidences of Predissociation

A number of intensity weakenings or breakoffs in the rotational structure of CO bands have been found and are reported in the literature. Those which are now considered by any investigator to indicate predissociation are listed in Table IV. In Table V are listed the energy levels of the supposed predissociation limits for no

TABLE IV. Intensity breakoffs in the rotational structure of CO bands.[28]

State	v	J	$J(J+1)$	cm^{-1} above $X^1\Sigma^+$	Band system
$A^1\Pi$	4[29]	26	702	71526.8	Angström $[B^1\Sigma^+\rightarrow A^1\Pi]$
		27	756	71608.3	
	7[30]	47	2256	77636.0	*IV* Positive $[A^1\Pi\rightarrow X^1\Sigma^+]$
		48	2352	77774.1	
	8[30]	36	1332	77509.2	*IV* Positive $[A^1\Pi\rightarrow X^1\Sigma^+]$
		37	1406	77613.6	
	9[30]	21	462	77479.4	*IV* Positive $[A^1\Pi\rightarrow X^1\Sigma^+]$
		22	506	77540.5	
	13[30,31]	16	282	81620	*IV* Positive $[A^1\Pi\rightarrow X^1\Sigma^+]$
$B^1\Sigma^+$	0[32]	37	1406	89655.2	Angström $[B^1\Sigma^+\rightarrow A^1\Pi]$
		38	1482	89801.3	
	1[33]	17	306	89598.0	Angström $[B^1\Sigma^+\rightarrow A^1\Pi]$
		18	342	89666.8	
$b^3\Sigma^+$	0[34,35]	55	3080	89950.6	*III* Positive $[b^3\Sigma^+\rightarrow a^3\Pi]$
		56	3192	90181.1	
	1[36]	42	1806	89768.3	*III* Positive $[b^3\Sigma^+\rightarrow a^3\Pi]$
		43	1892	89946.5	
$C^1\Sigma^+$	0[37]	28	812	93495.8	Herzberg $[C^1\Sigma^+\rightarrow A^1\Pi]$
		29	870	93607.9	
$c^3\Sigma^+$	0[38,39]	~27	~756	~93500	"3*A*" $[c^3\Sigma^+\rightarrow a^3\Pi]$

---

[23] D. P. Stevenson and J. A. Hipple, Phys. Rev. **62**, 237 (1942).

[24] A. G. Gaydon and W. G. Penney, Proc. Roy. Soc. London [A]**183**, 374 (1945).

[25] R. T. Birge and H. Sponer, Phys. Rev. **28**, 259 (1926).

[26] G. Herzberg, J. Chem. Phys. **10**, 306 (1942).

[27] A. G. Gaydon, Proc. Phys. Soc. **58**, 525 (1946).

[28] Where more than one rotational level is listed for a given vibrational state, the levels are the last of undiminished intensity and the first after the intensity breakoff.

[29] R. Schmid and L. Gerö, Physik. Zeits. **39**, 460 (1938).

[30] L. Gerö, Zeits. f. Physik **100**, 374 (1936).

[31] R. Schmid and L. Gerö, Zeits. f. physik. Chemie **B36**, 105 (1937).

[32] D. Coster and F. Brons, Nature **133**, 140 (1934); Physica 1, 155 (1934).

[33] R. Schmid and L. Gerö, Zeits. f. Physik **93**, 656 (1935).

[34] F. Brons, Nature **135**, 873 (1935).

[35] L. Gerö, Zeits. f. Physik **95**, 747 (1935).

[36] R. Schmid and L. Gerö, Zeits. f. Physik **96**, 198 (1935); L. Gerö, Zeits. f. Physik **101**, 311 (1936).

[37] R. Schmid and L. Gerö, Zeits. f. Physik **96**, 546 (1935).

[38] R. Schmid, Physik. Zeits. **37**, 55 (1936).

[39] L. Gerö, Zeits. f. Physik **109**, 210 (1938).

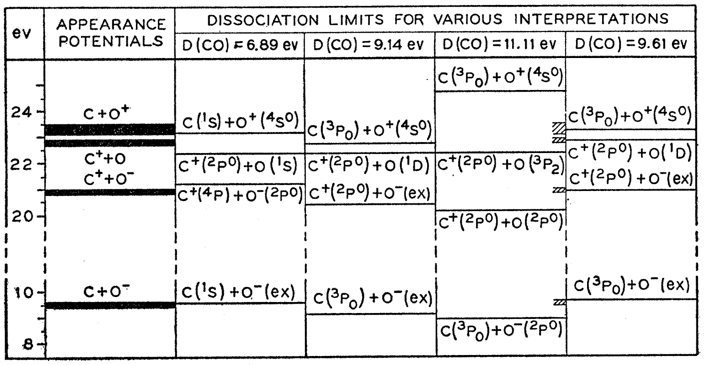

FIG. 3. An energy-level diagram showing the appearance potentials measured in electron-impact experiments and the closest dissociation limits for the appropriate ions predicted by four values of D(CO). D(CO) = 6.89, 9.14, and 11.11 ev are the values based on interpretations of the spectrum of CO currently supported in the literature (see Fig. 4). D(CO) = 9.61 ev is the value obtained from the interpretation of the band spectrum proposed in this paper and from the electron-impact experiments. The line widths in the appearance potential column indicate the limits of experimental error.

rotation ($J=0$) obtained from the data of Table IV.

The predissociations in $B^1\Sigma^+$ and $b^3\Sigma^+$ are thought both to be caused by the state $a'\,^3\Sigma^+$ whose vibrational levels converge to the same limit at 89620 cm^{-1}.[34, 35, 40] The vibrational levels of $a'\,^3\Sigma^+$ have been followed by perturbations in $A^1\Pi$ and $b^3\Sigma^+$ to $v=41$, 900 cm^{-1} from the convergence limit.[40]

Intensity breakoffs observed in the vibrational structures of various CO band systems have also been attributed to predissociation. In Table VI are listed such breakoffs as have been considered by Schmid and Gerö to be evidences of predissociation.[38, 31]

The three conflicting interpretations of the evidences of predissociation listed in Table IV now supported in the literature give D(CO) = 6.89, 9.14, and 11.11 ev. Several other values for D(CO) proposed on the basis of the CO spectrum have been withdrawn, are no longer supported, or are based on such scanty evidence as not to warrant further consideration. Each of the present interpretations will now be discussed.

Criticism of D(CO) = 6.89 ev

Schmid and Gerö[41, 31] consider all of the five effects listed in Table V to be true predissociations occurring at or just above dissociation limits of the molecule. The latest assignment of dissociation limits by Schmid and Gerö[29] is summarized in Table VII in which are also listed the vibrational breakoffs from Table VI. In Fig. 4 the assignment of dissociation limits is depicted graphically for comparison with other interpretations. The contention that D(CO) = 6.89 ev has recently been defended by Valatin.[42]

The $X^1\Sigma^+$ ground state is thought to dissociate into C(^1D)+O(^1D) at 81660 cm^{-1} in Schmid and Gerö's scheme. The lowest atomic term combination C($^3P_0$)+O($^3P_2$), however, is 55600 cm^{-1} (6.89 ev) above the ground molecular state. This specifies D(CO) as ordinarily defined.

Assignment of C(^5S)+O($^3P_0$) to the limit at 89620 cm^{-1} is used to calculate the excitation energy [C(^5S) − C($^3P_0$)] = 33800 cm^{-1}.[43] This was considered at the time the interpretation was proposed to be in passable agreement with the value 34994 cm^{-1} (4.34 ev) calculated by Bacher and Goudsmit[44] and the value 34000 cm^{-1} (4.2 ev) obtained by extrapolation by Edlén.[45] Shenstone has recently reported[46] the successful identification of intercombination lines with C(^5S) from which the level is now definitely fixed at 33735.2 cm^{-1} (4.16 ev) above C($^3P_0$).

A first objection to D(CO) = 6.89 ev is the fact that it cannot be reconciled with the results of electron-impact experiments. In Fig. 3 are plotted in the column headed D(CO) = 6.89 ev the dissociation limits of the appropriate ions closest to the observed appearance potentials, both divalent and tetravalent states of C and C$^+$ being considered.[47, 31] The ion O$^-$ is taken to exist either in

---

[40] R. Schmid and L. Gerö, Zeits. f. Physik **105**, 36 (1937); **106**, 205 (1937).

[41] R. Schmid and L. Gerö, Zeits. f. Physik **99**, 281 (1936).

[42] J. G. Valatin, J. Chem. Phys. **14**, 568 (1946); Nature **158**, 237 (1946).

[43] In Table VI, 89620 cm^{-1} is enclosed in parenthesis to emphasize that it is assumed and not related to the other levels by known excitation energies.

[44] R. F. Bacher and S. Goudsmit, Phys. Rev. **46**, 948 (1934).

[45] B. Edlén, Zeits. f. Physik **84**, 746 (1933).

[46] A. G. Shenstone, Phys. Rev. **72**, 411 (1947); see also B. Edlén, Nature **159**, 129 (1947).

[47] R. Schmid, Zeits. f. Physik **99**, 274 (1936).

its ground state, $^2P^0$, or in the excited state of very low binding energy, indicated O(*ex*), lying very close to the positive-energy continuum.[48] The electron affinity of O is taken to be 2.2 ev.[10, 12, 49] In two cases the dissociation limits and appearance potentials disagree by about 0.5 ev or more, and are thus considerably outside the limits of experimental error.

As pointed out by Herzberg[4] and others,[50] another grave objection to $D(\mathrm{CO}) = 6.89$ ev is the interpretation it places on the mechanism of the sublimation of carbon. $D(\mathrm{CO}) = 6.89$ ev gives for $L_1(\mathrm{C})$ the extremely low value 3.17 ev (73.1 kcal). To reach agreement with thermochemical measurements, it is necessary for Schmid and Gerö to assume[31] that carbon atoms come out of the solid in the tetravalent state, $\mathrm{C}(^5S)$, from which, even in equilibrium measurements, they cannot return to the ground state in the vapor outside the solid. This appears extremely unlikely in view of Shenstone's statement[46] that the existence of intercombination lines with $\mathrm{C}(^5S)$ "implies that ^5S can hardly be considered as a metastable state, and should not, therefore, enter in that role into thermochemical theory."

The results of Kenty *et al*, to be discussed later, in which the failure of Xe metastable atoms to dissociate CO in collisions of the second kind is taken to mean that $D(\mathrm{CO}) > 9.4$ ev, also provides evidence against Schmid and Gerö's interpretation of the band spectrum of CO.

TABLE V. Supposed predissociation limits ($J=0$) from intensity breakoffs in the rotational structure of CO bands.

State	v	cm^{-1} above $X^1\Sigma^+$
$A^1\Pi$	4	~71500[29]
$A^1\Pi$	7, 8, 9	77497±44[30]
$A^1\Pi$	13	>81620[30]
$B^1\Sigma^+$, $b^3\Sigma^+$	0, 1	89620±47[30]
$C^1\Sigma^+$, $c^3\Sigma^+$	0	<93550[37–39]

Criticism of $D(\mathrm{CO}) = 9.14$ ev

Herzberg[4] considers only the predissociations in $B^1\Sigma^+$ and $b^3\Sigma^+$ at 89620 cm^{-1} to occur at a dissociation limit of the molecule. The effect at 93550 cm^{-1} in $C^1\Sigma^+$ is thought to represent an upper limit for a dissociation limit as the predissociation occurs in one vibrational level only. Herzberg considers the slightness of the intensity drop in the (9, 18) IV Positive band and its extension over only two or three successive rotational levels to indicate an accidental predissociation or a perturbation.[51] This is also applied to the effects in the $v' = 7$ and 8 levels. Thus the effect at 77497 cm^{-1} in $A^1\Pi$ is thought to yield at most an upper limit for a dissociation limit. Although Herzberg has not commented upon the supposed predissociations at $v = 4$ and 13 of $A^1\Pi$ (see Table V), he must of necessity reject them.

Of the several possible choices for the states of excitation of the products at the 89620 cm^{-1} limit, Herzberg prefers $\mathrm{C}(^3P_0)+\mathrm{O}(^1D)$ giving $D(\mathrm{CO}) = 9.14$ ev (73750 cm^{-1}). This interpretation is summarized in Fig. 4.

Against the value $D(\mathrm{CO}) = 9.14$ ev may also be brought the charge that it does not satisfactorily account for the electron-collision experiments as Fig. 3 shows. It also is below the lower limit for $D(\mathrm{CO})$ indicated by the experiment of Kenty *et al* (see below). Furthermore, the evidences on which Herzberg based his interpretation of the effect in the (9, 18) IV Positive band are no longer as convincing as they might once have been. It has since been shown[52] that the intensity rise at the lines $P(25)$, $P(26)$, and $P(27)$ followed by a second intensity drop, is the result of the superposition of lines of the (0, 1) band of the so-called "3*A*" system ($c^3\Sigma^+ \rightarrow a^3\Pi$). Thus the intensity drop following $P(22)$ actually extends over several more rotational levels than was first supposed. Schmid and Gerö[31] report that on new plates the intensity breakoffs in $A^1\Pi$ at 77497 cm^{-1} show up as strongly as those in the Angström bands ($B^1\Sigma^+$). They present what appears to be a rather convincing argument that the effect can be neither an accidental predissociation nor an ordinary perturbation.

---

[48] Electron-collision experiments in both CO and NO appear to demonstrate the existence of this state. See references 10 and 12. It has been discussed theoretically by H. S. W. Massey, *Negative Ions* (Cambridge University Press, Teddington, England 1938) and by D. R. Bates and H. S. W. Massey, Phil. Trans. Roy. Soc. Lond. [A]**239**, 269 (1943).

[49] It should be noted that poorer agreement results from the choice of a larger value for the electron affinity such as that of D. T. Vier and J. E. Mayer, J. Chem. Phys. **12**, 28 (1944). Vier and Mayer's value is considered by the present writer to be erroneous.

[50] A. G. Gaydon, Proc. Phys. Soc. **58**, 704 (1946); L. H. Long and R. G. W. Norrish, Nature **158**, 237 (1946).

[51] This has since become subject to some revision as will be discussed below.

[52] R. Schmid and L. Gerö, Nature **139**, 928 (1937); L. Gerö, Zeits. f. Physik **109**, 210 (1938).

$D(\mathrm{CO})=9.14$ ev is in satisfactory agreement with thermochemical experiments.[4] The present writer feels that the real choice for $D(\mathrm{CO})$ now is between this value of 9.14 ev and that of 9.6 ev from electron-collision experiments.

Criticism of $D(\mathrm{CO})=11.11$ ev

The most recent contention that $D(\mathrm{CO})=11.11$ ev has been made by Gaydon and Penney.[24] The interpretation of the evidences of predissociation in the spectrum is essentially the same as that of Herzberg[4] except that the effect at 77497 cm^{-1} must now definitely be considered a perturbation. The choice of $\mathrm{C}(^3P_0)+\mathrm{O}(^3P_2)$ as the atomic term combination at 89620 cm^{-1} above $X^1\Sigma^+$ is based on a rigorous application of the noncrossing rule.[53]

Certainly the noncrossing rule has not been neglected in previous work as Gaydon and Penney seem to imply. Herzberg[54] and Herzberg and Mundie[55] have discussed several cases of predissociation in which the interaction between the vibrational levels of two states (whose potential curves cross in zero approximation) varies from "slight" to "strong." In a "slight" interaction ($^2\Sigma$ and $^2\Sigma$ in NO[55]) the two potential curves "almost cross." In a "strong" interaction two states are in effect produced ($^3\Pi_0$ and 0^+ in ICl).[56] This appears to cast considerable doubt on the basic assumption of Gaydon and Penney's argument, namely, that either a "crossing" occurs which always results in a strong interaction, or the states and dissociation limits are so situated that a crossing cannot occur at all.

The assumption of $D(\mathrm{CO})=11.11$ ev also fails to account for the electron-impact experiments (see Fig. 3). It is too large both to account for the bulk of the thermochemical results and the general conclusion that the Birge-Sponer extrapolation lies 20 to 40 percent too high for molecules like CO.[26,27]

4. PROPOSAL OF A NEW INTERPRETATION OF THE SPECTROSCOPIC EVIDENCE

Perhaps the most cogent argument against the present spectroscopic values for $D(\mathrm{CO})$ and in favor of $D(\mathrm{CO})=9.6$ ev from electron-impact experiments is the fact that it is possible to reinterpret the spectroscopic evidence to bring agreement with the electron-impact value. This new interpretation will now be proposed and its consequences discussed.

TABLE VI. Intensity breakoffs in the vibrational structure of CO bands.[29, 31, 38]

State	cm^{-1} above $X^1\Sigma^+$	Band system
$a^3\Pi$ $(v'=4)$	55400	Cameron $[a^3\Pi\rightarrow X^1\Sigma^+]$
$a'\,^3\Sigma$ $(v'=11)$	66500	Asundi $[a'\,^3\Sigma^+\rightarrow a^3\Pi]$
$d^3\Pi$	72000	Triplet $[d^3\Pi\rightarrow a^3\Pi]$
$C^1\Sigma^+$ $(v'=0)$	92000	Herzberg $[C^1\Sigma^+\rightarrow A^1\Pi]$
$c^3\Sigma^+$ $(v'=0)$	92000	"3A" $[c^3\Sigma^+\rightarrow a^3\Pi]$
$E^1\Sigma^+$ $(v'=0)$	93000	Hopfield-Birge $[E^1\Sigma^+\leftrightarrow X^1\Sigma^+]$

Effects at 9.61 and 11.60 ev

If $D(\mathrm{CO})$ is in fact 9.6 ± 0.1 ev, the lowest atomic-term combination of carbon and oxygen atoms, $\mathrm{C}(^3P_0)+\mathrm{O}(^3P_2)$, must lie 9.6 ± 0.1 ev above $v=0$, $J=0$ of $X^1\Sigma^+$. Thus the evidences of predissociation in the levels $v=7$, 8, and 9 of $A^1\Pi$ (see Table V) could be genuine. The limiting curve of dissociation, shown at the bottom of Fig. 5, is of the form for case *Ib* of predissociation.[55, 57] It places the limit for $J=0$ at 77500 cm^{-1} (9.61 ev) above $X^1\Sigma^+$. This assignment is in agreement with Schmid and Gerö's arguments as to the genuineness of this predissociation.[31] Acceptance of the assignment of $\mathrm{C}(^3P_0)+\mathrm{O}(^3P_2)$ to the level 77500 cm^{-1} (9.608 ev) places $\mathrm{C}(^1D)+\mathrm{O}(^3P_2)$ at 87692 cm^{-1} (10.87 ev), $\mathrm{C}(^3P_0)+\mathrm{O}(^1D)$ at 93368 cm^{-1} (11.58 ev), etc. These dissociation limits are plotted graphically in Fig. 4 in the column headed $D(\mathrm{CO})=9.61$ ev.

The effect at approximately 93550 cm^{-1} in $C^1\Sigma^+$ on this basis could also be a true predissociation. The 180 cm^{-1} between the dissociation limit and the intensity weakening is attributable to kinetic energy of the dissociation products. At the top of Fig. 5 is shown a possible limiting curve of dissociation drawn through the intensity breakoff and the $J=0$ intercept at 93368 cm^{-1} determined by the dissociation limit $\mathrm{C}(^3P_0)+\mathrm{O}(^1D)$. The slope of this limiting curve at the intensity breakoff is approximately 0.25 cm^{-1} giving 3.1A as the internuclear distance of the potential maxi-

---

[53] J. v. Neumann and E. Wigner, Physik. Zeits. **30**, 467 (1929).

[54] See reference 1, pp. 324ff and 449ff.

[55] G. Herzberg and L. G. Mundie, J. Chem. Phys. **8**, 263 (1940).

[56] W. G. Brown and G. E. Gibson, Phys. Rev. **40**, 529 (1932).

[57] See reference 1, pp. 428–464.

mum of the effective potential curve for $J=28$.[55, 57] Since r_e for $A^1\Pi$ is 1.23A,[58] this predissociation probably also belongs to case *Ib*. Although it appears likely on the basis of $D(\text{CO})=9.6\pm0.1$ ev that this effect and that at $v=7$, 8, 9 of $A^1\Pi$ are genuine predissociations, the interpretation would not be affected should they later be shown to be accidental predissociations or perturbations.

Effects at 8.86 and 10.12 ev

The intensity drop observed at low pressure by Schmid and Gerö[29] in $v=4$ of $A^1\Pi$, 8.86 ev above $X^1\Sigma^+$ cannot be accepted as a predissociation if $D(\text{CO})=9.61$ ev. The effect is observed only in the Q-branch and is the only one thought to be a predissociation in CO attributed to the *final* state of the emission bands in which it is found. No effect was found on the same plates at $v'=4$ in the IV Positive bands $[A^1\Pi\rightarrow X^1\Sigma^+]$. To explain this observation, Schmid and Gerö argue by analogy with a similar pressure effect in AlH that it should appear in the IV Positive bands only at appreciably lower pressures at which no plates were exposed. Schmid and Gerö feel that there is evidence of the effect at $v'=4$ of $A^1\Pi$ in some absorption spectrograms of Hopfield and Birge reproduced by Bonhoeffer and Harteck[59] which show an intensity minimum at 1400A ($v'=5$). All told, the effect does not appear to be so well established as a predissociation, however, that its rejection as such is critical. All the evidence pointing to $D(\text{CO})>9$ ev is also evidence against the interpretation of this effect as a predissociation.

Similarly, the effect in $v=13$ of $A^1\Pi$, 10.12 ev above $X^1\Sigma^+$, cannot be a genuine predissociation if $D(\text{CO})=9.61$ ev. The experimental evidence is Schmid and Gerö's failure to observe any rotational levels higher than $J=16$ even though some of the places where lines from such levels should appear were free of superpositions and were investigated carefully.[30, 31] $A^1\Pi$ is admittedly perturbed here so one cannot predict where the lines should be. In fact, Schmid and Gerö think perturbation to be the reason why the breakoff itself was not observed. Although the effect could be an accidental predissociation, it is more likely entirely the result of a perturbation. It cannot possibly be a genuine predissociation if *any* of the values proposed for $D(\text{CO})$ except that of Schmid and Gerö is correct.

Effect at 11.11 ev

The intensity weakenings which have been observed in $B^1\Sigma^+$ and $b^3\Sigma^+$ in the vicinity of 11.11 ev (see Table IV) have been accepted in every interpretation of the CO spectrum proposed to date as genuine evidences of predissociation. The limiting curve of dissociation, drawn by Gerö[30] and generally accepted, is shown in the middle section of Fig. 5, curve 1. The shape of the limiting curve and the fact that its slope at the ordinate axis is zero have been taken as evidence that the predissociation belongs to case *Ib*, putting a dissociation limit of the molecule 89620±47 cm⁻¹ above $X^1\Sigma^+$. This interpretation of the effect at 11.11 ev cannot represent the

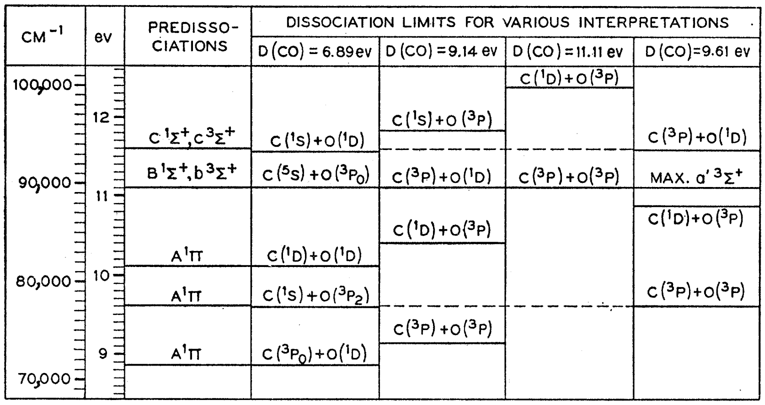

FIG. 4. An energy-level diagram showing the positions of five supposed evidences of predissociation in the spectrum of CO and their interpretation in terms of dissociation limits of the molecule. The interpretations giving $D(\text{CO})=6.89$, 9.14, and 11.11 ev are currently supported in the literature. $D(\text{CO})=9.61$ ev results from the interpretation proposed in this paper in agreement with the electron-impact experiments.

---

[58] H. Sponer, *Molekülspektren I. Tabellen* (Julius Springer, Berlin, 1935).

[59] K. K. Bonhoeffer and P. Harteck, *Grundlagen der Photochemie* (Dresden and Leipzig, 1933).

TABLE VII. Interpretation of predissociations in CO spectrum yielding $D(\text{CO}) = 6.89$ ev (Schmid and Gerö).

Dissociation products		Predissociations			
		Rotational breakoffs		Vibrational breakoffs	
States	cm^{-1} above $X^1\Sigma^+$	States	cm^{-1} above $X^1\Sigma^+$	State	cm^{-1} above $X^1\Sigma^+$
$\text{C}(^1S)+\text{O}(^1D)$	93115	$C^1\Sigma^+$; $c^3\Sigma^+$	<93550	$C^1\Sigma^+$; $c^3\Sigma^+$; $E^1\Sigma^+$	~ 92500
$\text{C}(^5S)+\text{O}(^3P_0)$	(89620)[43]	$B^1\Sigma^+$; $b^3\Sigma^+$	89620 ± 47		
$\text{C}(^3P_2)+\text{O}(^1D)$	89435				
$\text{C}(^1D)+\text{O}(^1D)$	81660	$A^1\Pi$	>81620		
$\text{C}(^1S)+\text{O}(^3P_0)$	77474	$A^1\Pi$	77497 ± 44		
$\text{C}(^3P_0)+\text{O}(^1D)$	71468	$A^1\Pi$	~ 71500	$d^3\Pi$	72000
$\text{C}(^1D)+\text{O}(^3P_2)$	65792			$a'\,^3\Sigma^+$	66500
$\text{C}(^3P_0)+\text{O}(^3P_2)$	55600			$a^3\Pi$	55400

facts if $D(\text{CO}) = 9.61$ ev for the closest dissociation limit then is $\text{C}(^1D)+\text{O}(^3P)$ at 10.87 ev.

It is suggested that $B^1\Sigma^+$ and $b^3\Sigma^+$ are predissociated at 11.11 ev by $a'\,^3\Sigma^+$ as has been supposed, but that $a'\,^3\Sigma^+$ has a potential curve with a maximum for no rotation. The dissociation limit of $a'\,^3\Sigma^+$ is then in all probability $\text{C}(^1D)+\text{O}(^3P)$ at 10.87 ev, requiring the maximum to be about 0.2 ev high. The vibrational levels under these circumstances converge to the energy of the maximum of the potential curve for $J=0$.

It is well known that such maxima in the potential curves of electronic states of molecules like CO are possible,[60] and considerable evidence for their existence has been found.[55, 56, 57] In this case the potential curve for $a'\,^3\Sigma^+$ could be formed by the "avoidance" of potential curves which in zero approximation are curves for a stable state having its dissociation limit at $\text{C}(^3P)+\text{O}(^1D)$, 11.58 ev above $X^1\Sigma^+$, and an unstable state with its dissociation limit at $\text{C}(^1D)+\text{O}(^3P)$, 10.87 ev above $X^1\Sigma^+$. The atomic-term combinations at these dissociation limits can each give rise to a $^3\Sigma^+$ state by the Wigner-Witmer correlation rules.

In an entirely different connection, Gaydon and Penney[24] have suggested that $a'\,^3\Sigma^+$ may possibly have a potential curve with maximum. It was mentioned as a way of sidestepping violation of the noncrossing rule entailed in the intersection of $a'\,^3\Sigma^+$ with the $^3\Sigma^+$ states from $\text{C}(^3P)+\text{O}(^3P)$ if $D(\text{CO}) < 11.11$ ev. However, Gaydon and Penney thought "the exact coincidence of this extrapolated limit at 11.11 ev with the energy of two known strong predissociations is too striking for this hypothesis to appear tenable," thus missing what is apparently the real significance of this coincidence.

Type of Predissociation at 11.11 ev

In the type of predissociation proposed here, the intersection of the potential curve of the state being predissociated ($B^1\Sigma^+$ or $b^3\Sigma^+$) with the potential curve of the state causing the predissociation ($a'\,^3\Sigma^+$) in all probability lies below the dissociation limits of both curves. In this way, the predissociation resembles that of case *Ib* classified by Herzberg.[57] However, as the state $a'\,^3\Sigma^+$, to which the nonradiative transition takes place and which later dissociates, has a potential curve with maximum, the limiting curve of dissociation should be of the form appropriate to case *I(c)* or case *III*. Thus the type of predissociation proposed here is properly not included in any of Herzberg's cases.

The limiting curve of dissociation for this type of predissociation is a straight line whose slope specifies the internuclear distance of the maximum of the potential curve causing the predissociation and not that of the intersection with the curve of the predissociated state. A strong interaction of the state causing the predissociation ($a'\,^3\Sigma^+$) with an unstable state is required to produce the potential curve with maximum whereas a weak interaction is required with the predissociated states ($B^1\Sigma^+$, $b^3\Sigma^+$). The radiationless transition from $B^1\Sigma^+$ into $a'\,^3\Sigma^+$ is an intercombination for which there seems to be evidence in the magnitude of the observed intensity weakening.[32]

Limiting Curve of Dissociation

A criterion for predissociation of the kind proposed here is that its limiting curve of dissociation must be a straight line having a slope which gives a reasonable value for the internuclear distance

---

[60] R. S. Mulliken, J. Phys. Chem. **41**, 5 (1937).

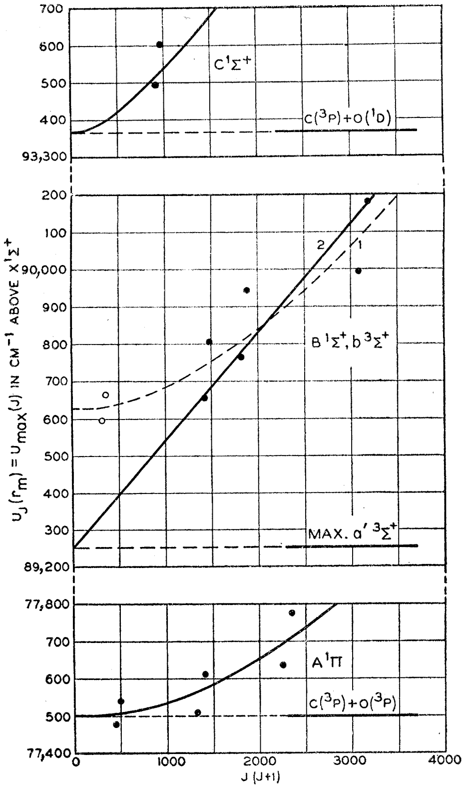

FIG. 5. Limiting curves of dissociation for predissociations observed in the spectrum of CO. The points plotted are the last rotational level of undiminished intensity and the first after the breakoff, between which the limiting curve must pass. In the bottom section of the figure the data for $v=9, 8, 7$ of $A^1\Pi$ are plotted (from left to right). In the middle section, similarly, the data for $v=1, 0$ of $B^1\Sigma^+$ and $v=1, 0$ of $b^3\Sigma^+$ are plotted. Curve 1 is that drawn by Gerö (reference 30). Curve 2 is that proposed in this paper. In the top section the data for the breakoff in $C^1\Sigma^+$ are plotted. The dissociation limits shown and the level marked *MAX.* $a'\,^3\Sigma^+$ are based on the interpretation proposed in this paper.

(r_m) at which the maximum occurs.[61] If all the intensity weakenings reported in $B^1\Sigma^+$ and $b^3\Sigma^+$ (Table IV) are accepted as predissociations by $a'\,^3\Sigma^+$, the straight line of maximum slope which can be drawn through the data gives $r_m=3.9$A. This value is impossibly high for states of a molecule like CO with covalent binding since the potential curves must lie very close to their asymptotes at such an internuclear distance. However, it is to be observed that the four evidences of predissociation at 11.11 ev are not equally credible as such. The breakoffs in $v'=0$ of $B^1\Sigma^+$ and $v'=1$ of $b^3\Sigma^+$ observed in the P, Q, and R-branches of the bands are good examples of predissociations and can hardly be questioned. Similarly, the predissociation in $v'=0$ of $b^3\Sigma^+$ appears well founded. The effect in $v'=1$ of $B^3\Sigma^+$, on the other hand, was observed by Schmid and Gerö[33] only in the P-branch of the (1, 0) and the Q-branch of the (1, 1) Angström bands despite considerable overlapping of lines from CO^+ and CO_2 bands. Coster and Brons,[32] although they looked for such an effect, could not find it because of the presences of crowded lines of CO_2. If this effect, indicated by open circles in Fig. 5, is considered to be an accidental predissociation, a perturbation, the result of superposition of other band lines, or predissociation by a state other than $a'\,^3\Sigma^+$, one can draw a straight line through the remaining data (curve 2 in Fig. 5) of maximum slope giving $r_m=2.9$A. Since the maximum of the potential curve is low and broad (see Fig. 6), one would not expect any observable leakage through it.

Although the effect in $v'=1$ of $B^1\Sigma^+$ may well be predissociation by a state other than $a'\,^3\Sigma^+$, interpretation of such an effect as something other than predissociation is not without precedent. Two other effects in the spectrum of CO, once thought to indicate predissociation, have been shown to be spurious. A second weakening in the rotational structure of $v=9$, $A^1\Pi$ at $P(28)$,[30] as mentioned earlier, is now known to result from a superposition of lines from the (0, 1) band of the "3A" system on the lines $P(25)$, $P(26)$, $P(27)$ preceding it.[52] The sudden ending of the rotational structure of $v=10$, $A^1\Pi$ at $P(16)$ and $Q(17)$ observed by Brons[62] was later shown by Gerö[63] to be the effect of insufficient exposure of the plates causing the perturbation of $A^1\Pi$ by a $^3\Sigma^+$ state to look like a predissociation. Gerö points out how easily one may be misled in considering a sudden intensity decrease as a predissociation if the initial state is perturbed. With insufficient exposure, the perturbed lines disappear as they are generally weaker than the unperturbed lines. If the plates are overexposed, on the other hand,

---

[61] The effective potential curve is represented by $U_J(r)=U_0(r)+(h/8\pi^2c\mu r^2)J(J+1)$. (See reference 55.) The limiting curve is $U_J(r_m)=U_0(r_m)+(h/8\pi^2c\mu r_m^2)J(J+1)$. Its slope is thus $h/8\pi^2c\mu r_m^2$ and its intercept at the ordinate axis is $U_0(r_m)$. This latter gives the energy level of the maximum in the rotationless potential curve above the ground molecular state.

[62] F. Brons, Physica **2**, 1108 (1935).

[63] L. Gerö, Zeits. f. Physik **99**, 52 (1936).

one is bothered by superpositions of band lines from other molecules. These comments are also pertinent to the interpretation of the effects in the spectrum 8.86 and 10.12 ev above $X^1\Sigma^+$ (see above).

Inasmuch as the $v=1$, $J=0$ level $B^1\Sigma^+$ lies at about 89100 cm^{-1}, which is below curve 2 of Fig. 5, one would expect predissociation to commence in one of the lower rotational levels. Failure to observe it may well be the result of the superposition of CO$^+$ and CO$_2$ lines known to be present. Furthermore, predissociation by $a'\ {}^3\Sigma^+$ requires an intercombination interaction which is not very intense in the first place.

Potential Curve of $a'\ {}^3\Sigma^+$

The question now arises as to whether a potential curve for $a'\ {}^3\Sigma^+$ which possesses a maximum approximately 0.2 ev above its asymptote and at a nuclear separation of 2.9A or greater is at all reasonable. Since the dissociation energy of CO in the $a'\ {}^3\Sigma^+$ state is certainly greater than 4 ev, a maximum only 0.2 ev high may be expected to lie at an internuclear distance quite large with respect to r_e. Enough is known about the molecular constants of $a'\ {}^3\Sigma^+$, however, to make a more detailed investigation possible.

Schmid and Gerö[40] have determined the rotational constant, B_e, of $a'\ {}^3\Sigma^+$ to be about 1.31 cm^{-1} from which $r_e=1.37$A. The frequency ω_e is given as 1180 cm^{-1} (see also Sponer[58]). Assuming $a'\ {}^3\Sigma^+$ in zero approximation (no interaction with an unstable state) to become asymptotic to the limit at C(^3P)+O(^1D), one can calculate by the Morse function the potential curve plotted in Fig. 6. $v=0$, $J=0$ of $a'\ {}^3\Sigma^+$ is 55380 cm^{-1} above $X^1\Sigma^+$.[40] The avoidance of crossing of this potential curve with that of an unstable state from C(^1D)+O(^3P) can produce a resulting potential curve having a maximum of the proper height and at an internuclear distance of greater than 3A as the construction in Fig. 6 shows.

The objection may immediately be raised that the Morse function could lie considerably below the true potential curve near its asymptote. This would mean that the maximum actually lay at a smaller value of r than shown in Fig. 6. However, there are two considerations which indicate that the state of affairs depicted in Fig. 6 is not seriously in error and may in fact predict too small a value of r_m. The first of these is the fact that the r_e calculated from Schmid and Gerö's B_e for $a'\ {}^3\Sigma^+$ may be low. Using the relation $\omega_e r_e^2=$constant, known to hold approximately for the states of a given molecule,[64] with an average constant evaluated from the ω_e and r_e of well known states of CO, one calculates $r_e=1.52$ cm^{-1}. This is significant because ω_e for $a'\ {}^3\Sigma^+$ is undoubtedly much more accurate than B_e. The second consideration is the fact that the Morse function does in all probability provide a good approximation for this particular case. Lotmar[65] and Coolidge, James, and Vernon[66] agree that more accurate representations of potential curves such as those of Rosen-Morse and Pöschl-Teller

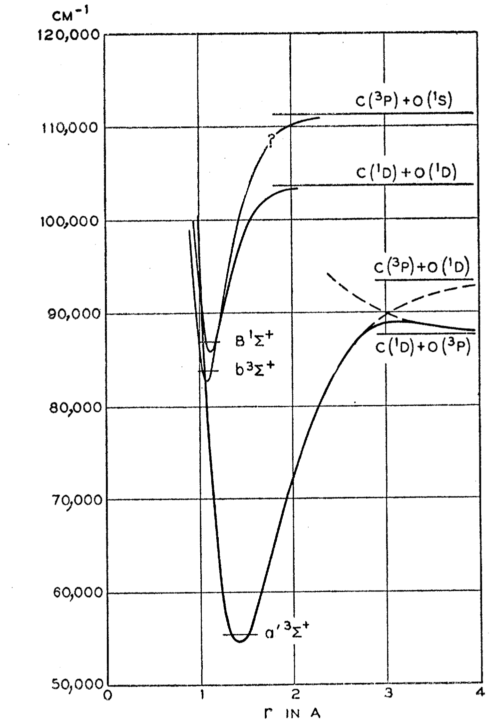

FIG. 6. Potential curves of the electronic states involved in the predissociation at 11.11 ev. The curve for $a'\ {}^3\Sigma^+$ is formed from the avoidance of curves for a stable and an unstable state. The curve for the stable state is plotted from a Morse function and the curve of the unstable state drawn so as to produce a maximum of the resulting curve 89250 cm^{-1} above $X^1\Sigma^+$. The curves for $B^1\Sigma^+$ and $b^3\Sigma^+$ are also plotted from Morse functions. The question mark indicates that the dissociation limit of $b^3\Sigma^+$ is uncertain (reference 68). The positions of the dissociation limits are those given by the interpretation proposed in this paper.

---

[64] See reference 1, p. 498.

[65] W. Lotmar, Zeits. f. Physik **93**, 528 (1934/35).

[66] A. S. Coolidge, H. M. James, and E. L. Vernon, Phys. Rev. **54**, 726 (1938).

reduce to the Morse function if $(D/\delta)^{\frac{1}{2}}=1$. D is the distance from minimum to asymptote and $\delta=3\omega_e(B_e)^{\frac{3}{2}}/(\alpha_e\omega_e+6B_e^2)$. Admittedly B and certainly α_e are not known very well for $a'\ {}^3\Sigma^+$. However, taking $D=38580$ cm, $\omega_e=1180$ cm^{-1}, $B_e=1.31$ cm^{-1}, and determining $\alpha_e=0.014$ cm^{-1} from the relation[67] $\alpha_e/B_e\approx 1.4\omega_e x_e/\omega_e$ with $\omega_e x_e=9$ cm^{-1} from Sponer,[58] one calculates $(D/\delta)^{\frac{1}{2}}=0.99$.

The maximum in the potential curve of $a'\ {}^3\Sigma^+$ would on the above considerations lie at an internuclear distance approximately twice the equilibrium internuclear distance r_e. $r_m=2r_e$ has been suggested by Herzberg and Mundie[55] as an approximate upper limit for the r value of a maximum of a rotationless curve.

In Fig. 6 are also plotted the potential curves of $B^1\Sigma^+$ and $b^3\Sigma^+$ which are predissociated by $a'\ {}^3\Sigma^+$.[68] Within the limits of accuracy of the diagram, it is seen that the intersections demanded by the Franck-Condon principle can occur. There is perhaps some further evidence here also that the value of r_e for $a'\ {}^3\Sigma^+$ in Fig. 6 is a little low.

Curve 2 of Fig. 5 is the straight line of maximum slope which can be drawn between the two data points[28] for each of the three predissociations accepted as such. Should the maximum in the potential curve of $a'\ {}^3\Sigma^+$ lie somewhat higher than the 2.9A predicted by this line, the limiting curve would be a line of less slope passing easily through the experimental points.

In the preliminary report of this work[5] it was suggested that if the stopping of the rotational structure in $v=0$ of $b^3\Sigma^+$ (see Table IV) were the result of something other than predissociation by $a'\ {}^3\Sigma^+$ one could draw a straight line limiting curve through the two remaining sets of points having a slope which gives r_m as small as 2.1A. The interpretation can be carried out satisfactorily, it appears, without this assumption.

Consequences and Comparison with Other Interpretations

For $D(\text{CO})=9.61$ ev the position with respect to the interpretation of effects in the spectrum as genuine or accidental predissociations, perturbations, or other effects is no less tenable than that required by $D(\text{CO})=9.14$ ev, now widely accepted. The interpretation of the effects at 8.83 and 10.12 ev must be the same. As opposed to the interpretation of the breakoff in $v=0$ of $C^1\Sigma^+$ at 11.60 ev as an upper limit for a predissociation and those in $v'=7$, 8, and 9 of $A^1\Pi$ at 9.61 ev as accidental predissociations or perturbations if $D(\text{CO})=9.14$ ev, only a single breakoff, namely that in $v'=1$ of $B^1\Sigma^+$ at 11.11 ev, need be reinterpreted if $D(\text{CO})=9.61$ ev.

In Herzberg's energy level diagram of the CO molecule[69] the dissociation limits of a number of electronic states are drawn under the assumption $D(\text{CO})=9.14$ ev. It would appear that no difficulty is encountered if all these limits are raised by the 0.47 ev demanded if $D(\text{CO})=9.61$ ev. Schmid and Gerö's data[31, 40, 70] on the convergence of vibrational levels in $a^3\Pi$, $d^3\Pi$, and $e^3\Sigma^-$ are not in conflict with the new energy level scheme. However, the convergence of $I^1\Sigma^-$, known only through its perturbation of $A^1\Pi$,[40] cannot be fitted to the new scheme. There is no limit corresponding to two singlet atomic terms close enough to the supposed convergence. If the state were not a singlet as is now supposed,[71] there would be no such difficulty.

Some of the intensity breakoffs in the vibrational structure of CO bands listed in Table V cannot be attributed to predissociation if $D(\text{CO})=9.61$ ev. Their explanation may equally well be found in the Franck-Condon principle.

Finally, $D(\text{CO})=9.61$ ev is in satisfactory agreement with all data bearing on $D(\text{CO})$ and $L_1(\text{C})$ from sources other than electron impact and the band spectrum. These results will now be discussed.

5. PHOTO-DISSOCIATION OF CO

In 1938, Faltings, Groth, and Harteck[72] demonstrated that CO is dissociated by the Xe resonance line 1295A forming CO_2 with quantum yield unity. This was interpreted to mean that $D(\text{CO})\leqq 221$ kcal (9.57 ev), with which interpretation Herzberg has agreed.[26] The failure of

---

[67] See reference 1, p. 114.

[68] The data for the Morse functions in these cases were obtained from Sponer's tables (reference 58) except that $r_e=1.09$A was used for $b^3\Sigma^+$. This was calculated from a more recent value of the rotational constant, $B_e=2.075$ cm^{-1} reported in R. Schmid and L. Gerö, Zeits. f. Physik **96**, 198 (1935).

[69] See reference 1, Fig. 174, p. 481.

[70] L. Gerö and R. Schmid, Zeits. f. Physik **112**, 676 (1939).

[71] R. Schmid and L. Gerö, Zeits. f. Physik **94**, 386 (1935).

[72] K. Faltings, W. Groth, and P. Harteck, Zeits. f. physik. Chemie **B41**, 15 (1938).

the line 1470A to dissociate CO was taken to mean $D(\mathrm{CO}) \geqq 194$ kcal (8.43 ev).

Gaydon and Penney,[73] however, object to the interpretation giving $D(\mathrm{CO}) \leqq 9.57$ ev on the grounds that the only lines in the known absorption bands of CO (IV Positive) in the vicinity of 1295A correspond to transitions from rotational or vibrational levels very sparsely populated at room temperature. They propose a mechanism of the photo-dissociation involving absorption of the quantum (1295A) to form $\mathrm{CO}(A^1\Pi)$, which, on collision with $\mathrm{CO}(X^1\Sigma^+)$, forms $\mathrm{CO_2}$ and C. On this basis no conclusion concerning $D(\mathrm{CO})$ may be drawn from the experiments.

To Gaydon and Penney's picture of the photochemical decomposition of CO Schmid and Gerö[74] raise the rather similar objections that, considering line half-widths, the accuracy of coincidence of the line 1295A with the closest line of the IV Positive system [$Q(38)$ of the (10, 0) band] is not sufficient; that the probability of exciting this line is only 0.0001 percent by the Boltzmann distribution law; and that a single absorption line, even if it coincided properly, could not absorb 70 percent of the strongly broadened Xe line, as observed in the photochemical experiments. Schmid and Gerö feel that absorption by a continuum must be assumed and link the process to the continuum they believe begins at the predissociation limit 77497 cm^{-1} above $X^1\Sigma^+$. It is shown that enough transitions can occur from higher, but sufficiently well populated, rotational states in $v=0$ of $X^1\Sigma^+$ to account for the experimental results. Failure to observe a continuous absorption in this region at rather low resolving power is attributed to the narrowness of the "effective region" in the continuum and the low transition probability into the continuum evidenced by the extent and magnitude of the predissociation in $A^1\Pi$. In rebuttal, Gaydon[75] refers again to the failure to observe continuous absorption near 1295A and expresses his opinion that line broadening may be sufficient to make absorption by a single band line possible.

$D(\mathrm{CO}) = 9.6$ ev may be reconciled with either the interpretation of the photodissociation of CO proposed by Gaydon and Penney or that proposed by Schmid and Gerö. The latter argument is unaffected by a change in the assignment of dissociation products to the dissociation limit. Of the two, Schmid and Gerö's interpretation is perhaps preferable in the light of the interpretation of the band spectrum proposed in this paper. The objections to the conclusions of Faltings, Groth, and Harteck agreed to by Herzberg appear adequate.

6. DISSOCIATION OF CO BY METASTABLE ATOMS

Recently, Kenty, Aicher, Noel, Paritsky, and Paolino[76] have observed some new bands in the green, excited in a mixture of xenon and oxygen, which, if the source of the bands and mode of their excitation are correctly interpreted, provide independent evidence of a lower limit for $D(\mathrm{CO})$. That the bands are emitted by $\mathrm{O_2}$ is evident from the fact that they are produced when $\mathrm{O_2}$ itself or gases such as $\mathrm{CO_2}$ and $\mathrm{H_2O}$, from which $\mathrm{O_2}$ may be produced by dissociation by metastable Xe atoms, are admitted to the Xe discharge. The bands are not produced in mixtures of Xe with $\mathrm{N_2}$, $\mathrm{H_2}$ or $\mathrm{CH_4}$. The mode of excitation of the new band system is thought to be a resonant-energy exchange between the metastable Xe atom and the $\mathrm{O_2}$ molecule. Failure of the bands to appear with a CO admixture is taken as evidence that $D(\mathrm{CO})$ is greater than the excitation energy of the higher metastable state of Xe, 9.4 ev. Taken at face value this result does provide additional evidence for discrimination among the several proposed values of $D(\mathrm{CO})$. Only $D(\mathrm{CO}) = 9.61$ ev and 11.11 ev are allowed.

7. ELECTRON COLLISION EXPERIMENTS IN $\mathrm{CH_4}$ AND $\mathrm{CS_2}$

Ionization and dissociation processes have been observed in electron-impact studies of $\mathrm{CH_4}$ and $\mathrm{CS_2}$ in which, one can be quite certain, all the bonds are broken and the molecule completely fragmented. These processes are:

(1) $\mathrm{CH_4}+\epsilon^- \rightarrow \mathrm{H}^+ + \mathrm{C} + 3H + 2\epsilon$
$\mathrm{A}(\mathrm{H}^+) = 29.4 \pm 0.6$ ev

(2) $\mathrm{CH_4}+\epsilon^- \rightarrow \mathrm{C}^+ + 4\mathrm{H} + 2\epsilon^-$
$\mathrm{A}(\mathrm{C}^+) = 26.7 \pm 0.7$ ev

(3) $\mathrm{CH_4}+\epsilon^- \rightarrow \mathrm{C}^- + \mathrm{C}^+ + 3\mathrm{H} + \epsilon^-$
$\mathrm{A}(\mathrm{C}^-) = 27.4 \pm 0.6$ ev

(4) $\mathrm{CS_2}+\epsilon^- \rightarrow \mathrm{C}^+ + 2\mathrm{S}$
$\mathrm{A}(\mathrm{C}^+) = 21.5 \pm 1.0$ ev

---

[73] A. G. Gaydon and W. G. Penney, Nature **150**, 406 (1942).

[74] R. F. Schmid and L. Gerö, Proc. Phys. Soc. **58**, 701 (1946).

[75] A. G. Gaydon, Proc. Phys. Soc. **58**, 704 (1946).

[76] C. Kenty, J. O. Aicher, E. B. Noel, A. Paritsky, and V. Paolino, Phys. Rev. **69**, 36 (1946).

(1), (2), and (3) were observed by Smith,[77] (4) by Smyth and Blewett.[78] Processes like these are not very probable, making measurement of their onset potentials difficult. This accounts for the rather wide limits of error. In each case the calculation of an upper limit for L_1(C) from the onset potential has been possible as the appropriate heat of formation, ionization energy (electron affinity, if needed), and dissociation energy are known.

Smith has done this for (1), (2), and (3), Lozier[12] for (4). The results are:

(1) $L_1(\mathrm{C}) \leqq 6.1 \pm 0.6$ ev or 141 ± 14 kcal,
(2) $L_1(\mathrm{C}) \leqq 5.7 \pm 0.7$ ev or 131 ± 16 kcal,
(3) $L_1(\mathrm{C}) \leqq 6.0 \pm 0.9$ ev or 139 ± 21 kcal,
(4) $L_1(\mathrm{C}) \leqq 5.8 \pm 1.0$ ev or 134 ± 23 kcal.

The reason these values were considered upper limits only is that the kinetic energy of the fragments in the processes are not known. If L_1(C) is actually less than these values, the activation energies of the processes inverse to each of the four processes must be very nearly the same. As this appears unlikely, it seems more reasonable to assume that ions can be formed at rest in each process. The results quoted above agree better with $L_1(\mathrm{C}) = 5.9$ ev (136 kcal) corresponding to $D(\mathrm{CO}) = 9.6$ ev than with any other value proposed for L_1(C).

8. DISSOCIATION ENERGIES OF CO+ AND CN

The dissociation energy of CO^+ can be determined from the cycle $I(\mathrm{CO}) + D(\mathrm{CO}^+) = D(\mathrm{CO}) + I(\mathrm{C})$. I(C) is known to be 11.27 ev. I(CO) has been determined by electron-collision experiments as 14.1 ± 0.1 ev.[10, 79] (See also Fig. 2.) This value in all probability represents the distance from $v=0$ of $\mathrm{CO}(X^1\Sigma^+)$ to $v=0$ of $\mathrm{CO}^+(X^2\Sigma)$ as the internuclear separations for these states are 1.13A and 1.114A,[58] respectively, and the width of the Franck-Condon region is about 0.1A. From these ionization potentials one obtains $D(\mathrm{CO}^+) = D(\mathrm{CO}) - 2.8$ ev. With $D(\mathrm{CO}) = 9.6$ ev, $D(\mathrm{CO}^+) = 6.8$ ev.

Gaydon and Penney[24] have discussed what is known of the electronic states and dissociation limits of CO^+. Their scheme of dissociation limits is in agreement with $D(\mathrm{CO}^+) = 6.8$ ev if the limit of $B^2\Sigma$ is $\mathrm{C}^+(^2P) + \mathrm{O}(^1D)$ at 8.8 ev. This seems reasonable in view of the extrapolation by Biskamp[80] of vibrational levels of $B^2\Sigma$ to 9.3 ev above $X^2\Sigma$. $v=0$ of $B^2\Sigma$ lies at 5.66 ev and its vibrational levels are known to 7.46 ev above the ground state. Biskamp's linear extrapolation for the ground state, $X^2\Sigma$, puts its limit at 9.9 ev. Since the extrapolation is a long one from the highest known level at 3.2 ev, its relation to the actual limit $\mathrm{C}^+(^2P) + \mathrm{O}(^3P)$ at 6.8 ev is not surprising.

Herzberg[4] has calculated the relation $D(\mathrm{CN}) = D(\mathrm{CO}) - 3.18$ ev from a cycle involving thermochemical and spectroscopic quantities.[2] He has more recently given compelling reasons for preferring the value[81] of the dissociation energy of $\mathrm{C_2N_2}$ into 2CN used in his original calculation to a newer value of White.[82] With $D(\mathrm{CO}) = 9.61$ ev, $D(\mathrm{CN}) = 6.43$ ev. The only independent evidence concerning D(CN) comes from rather long extrapolations of vibrational levels. Gaydon[27] gives 9.9 ev as the result of a linear Birge-Sponer extrapolation. Schmid, Gerö and Zemplén[83] think the ground state $\mathrm{CN}(X^2\Sigma)$ converges to 7.5 ev with the lowest atomic term combination lying considerably lower. Neither of these results is in disagreement with the conclusion $D(\mathrm{CN}) = 6.43$ ev. On the other hand, Schmid, Gerö and Zemplén's contention that the $\mathrm{CN}(A^2\Pi)$ converges to 7.50 ± 0.12 ev and $\mathrm{CN}(B^2\Sigma)$ to 8.12 ± 0.12 ev cannot be reconciled with the present interpretation. There is no direct contradiction of experimental data involved, however.

The spectra of CO^+ and CN thus provide no direct evidence for or against $D(\mathrm{CO}) = 9.61$ ev, nor in fact any basis for preferring it over $D(\mathrm{CO}) = 9.14$ ev. Either value of D(CO) provides an adequate basis for interpretation.

9. THERMOCHEMISTRY OF CARBON

The value $D(\mathrm{CO}) = 9.61$ ev demands no change in the general interpretation of the thermochemistry of carbon supported by Herzberg.[4, 26] The thermochemical evidence is not definite enough

---

[77] L. G. Smith, Phys. Rev. **51**, 263 (1937).

[78] H. D. Smyth and J. P. Blewett, Phys. Rev. **46**, 276 (1934).

[79] J. T. Tate and P. T. Smith, Phys. Rev. **39**, 270 (1932).

[80] H. Biskamp, Zeits. f. Physik **86**, 33 (1933).

[81] G. B. Kistiakowsky and H. Gershinowitz, J. Chem. Phys. **1**, 432 (1933).

[82] J. U. White, J. Chem. Phys. **8**, 459 (1940).

[83] R. Schmid, L. Gerö and J. Zemplén, Proc. Phys. Soc. **50**, 283 (1938).

to distinguish values of $L_1(\mathrm{C})$ as close as 125 and 136 kcal. However, what indications there are point to a value higher than that supported by Herzberg. Goldfinger and Jeunehomme,[84] in a paper which reviews the thermochemical evidence available at the time, calculated vapor-pressure curves for $L_1(\mathrm{C})=170.2$, 124.8, and 108.3 kcal, corresponding to $D(\mathrm{CO})=11.11$, 9.14, and 8.41 ev, respectively.[2] These were compared with the experimental results of direct measurements of the vapor pressure of carbon. Most of the data lay between the curves calculated for $L_1(\mathrm{C})=170.2$ and 124.8 kcal. However, the latter value was considered correct on the grounds of Herzberg's value for $D(\mathrm{CO})$. As has been pointed out before,[10] $D(\mathrm{CO})=9.6$ ev giving $L_1(\mathrm{C})=136$ kcal is in better agreement with the vapor pressure measurements. Duchesne, Goldfinger and Rosen[85] have stated that the more recent measurements of the vapor pressure of carbon by Ribaud and Bégue[86] similarly are too high for $L_1(\mathrm{C})=170$ kcal and too low for $L_1(\mathrm{C})=125$ kcal.

10. OTHER EVIDENCE

Arguments favoring $L_1(\mathrm{C})=170$ kcal have been presented by several investigators but appear to have been successfully refuted by others. Baughan's objections[87] to the low C–H bond energy calculated from $L_1(\mathrm{C})=125$ kcal have been answered by Herzberg[26] and Long and Norrish.[16] The agreement by Kynch and Penney's calculation[88] of the long wave length limits of absorption spectra in benzene, butadiene, and hexatriene on the basis of $L_1(\mathrm{C})=170$ kcal with the observed limits is considered fortuitous by Herzberg,[26] and to provide no basis for deciding on $L_1(\mathrm{C})$ by Mulliken and Rieke.[89] The calculation is also criticized by Long and Norrish[16] and by Duchesne, Goldfinger and Rosen.[85] Sidgwick and Springall's support[90] for $L_1(\mathrm{C})=170$ kcal, found in the calculation of Hg–C bond energies in several molecules, is questioned by Long and Norrish.[91] In none of this does there appear any convincing evidence against a value of 136 kcal for $L_1(\mathrm{C})$.

Long and Norrish in their general review of the thermochemistry of carbon[16] accept the value $L_1(\mathrm{C})=125$ kcal. They feel they have evidence, however, that $L_2(\mathrm{C})$, the heat of sublimation into tetravalent carbon $\mathrm{C}(^5S)$, is approximately 190 kcal making $L_2(\mathrm{C})-L_1(\mathrm{C})\sim 65$ kcal. This is unacceptable to Shenstone and Edlén,[46] on the basis of the recent fixing of the $\mathrm{C}(^5S)$ excitation energy at 96.4 kcal (33735.2 cm^{-1}). The argument of Long and Norrish thus seems to need fundamental revision. It certainly cannot be used against a somewhat higher value of $L_1(\mathrm{C})$. The use of Shenstone's excitation energy for $\mathrm{C}(^5S)$ makes $L_2(\mathrm{C})=232.1$ kcal.

Finally, the calculation of Duchesne, Goldfinger and Rosen[85] should be mentioned. It yields the value $D(\mathrm{CO})=9.4$ ev $[L_1(\mathrm{C})=132\text{ kcal}]$ which is independent of spectroscopic data on the CO molecule. This result is as good if not better evidence for $D(\mathrm{CO})=9.61$ ev as for $D(\mathrm{CO})=9.14$ ev.

11. CONCLUSION

It has been the purpose of this paper to show that a satisfactory interpretation of all the relevant data can be made only if the value of the dissociation energy of carbon monoxide is 9.61 ev. As consequences of this position we obtain the values

$$\begin{aligned} D(\mathrm{CO}) &= 9.608 \text{ ev} = 77500 \text{ cm}^{-1},\\ L_1(\mathrm{C}) &= 5.887 \text{ ev} = 135.7 \text{ kcal},\\ L_2(\mathrm{C}) &= 10.07 \text{ ev} = 232.1 \text{ kcal},\\ D(\mathrm{CO}^+) &= 6.8 \text{ ev},\\ D(\mathrm{CN}) &= 6.43 \text{ ev}. \end{aligned}$$

---

[84] P. Goldfinger and W. Jeunehomme, Trans. Faraday Soc. **32**, 1591 (1936).

[85] J. Duchesne, P. Goldfinger, and B. Rosen, Nature **159**, 130 (1947).

[86] G. Ribaud and J. Bégue, Comptes Rendus **221**, 73 (1945).

[87] E. C. Baughan, Nature **147**, 542 (1941).

[88] G. J. Kynch and W. G. Penney, Proc. Roy. Soc. London [A]**179**, 214 (1941).

[89] R. S. Mulliken and C. A. Rieke, Rev. Mod. Phys. **14**, 259 (1942).

[90] N. V. Sidgwick and H. D. Springall, Nature **156**, 599 (1945).

[91] L. H. Long and R. G. W. Norrish, Nature **157**, 486 (1946).