

ON A DISSOCIATION SCHEME FOR THE SPECTRUM OF CO⁺ *

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ABSTRACT. A dissociation scheme has been proposed for the spectrum of CO⁺ and correlated with the convergence limits of the known spectroscopic states. For the energy of dissociation of CO⁺ the values 5.58 and 7.92 volts have been considered likely according as the products of dissociation are C⁺ (²P) + O(³P) and C(³P) + O⁺(⁴S) respectively.

In a recent paper the author (Sen Gupta, 1951) has shown that the use of the value $D(\text{CO}) = 8.87$ volts explains satisfactorily the predissociation effects in the spectrum of CO and the results of the experiments on the sublimation of graphite. As the energy of dissociation of CO⁺ is closely interrelated with that of CO, an attempt is made here to find out whether a dissociation scheme with the assignment of $D(\text{CO}) = 8.87$ volts is able to account for the observed effects in the spectrum of CO⁺.

For CO⁺, three band systems are known, *viz.*,

First negative : $B \ ^2\Sigma^+ \rightarrow X \ ^2\Sigma^+$

Comet tail : $A \ ^2\Pi \rightarrow X \ ^2\Sigma^+$

Baldet-Johnson : $B \ ^2\Sigma^+ \rightarrow A \ ^2\Pi$

The data so far available are given in the following Table.

TABLE I

(Sponer, 1935 ; Biskamp, 1933)

State	Energy height above ground state in volts	Vibrational levels observed		Extrapolated convergence limits	
		Number	Energy height above $v=0$ in volts	above $v=0$ of state. in volts	Above ground state. in volts
$X \ ^2\Sigma^+$	0	$v=13$ ($v=33$)	3.21 (6.90)	9.90	9.90
$A \ ^2\Pi$	2.53	$v=14$	2.50	~4.8	~7.33
$B \ ^2\Sigma^+$	5.66	$v=10$	1.80	3.70	9.36

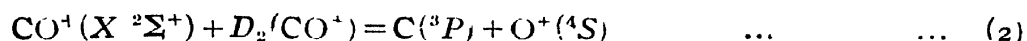
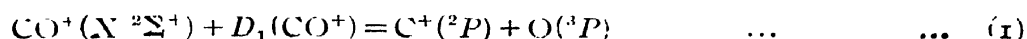
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The location of the convergence limit of the ground state $X^2\Sigma^+$, is most important, but it will be seen that only a few vibrational levels have been observed. Biskamp's (1933) linear extrapolation, yielding 9.9 volts for this limit covers an unknown region of about two-thirds of this value and can be regarded only as an upper limit for the energy of dissociation. Other investigators (Biskamp, 1933; Asundi and Samuel, 1937; Asundi, 1943; Gaydon and Penney, 1945) have made use of the extrapolated value 9.9 in their discussions, but it is felt that the extrapolation is too long for this value to be reliable. For molecules of this type Gaydon (1946) has given some examples showing that the Birge-Sponer extrapolation is about 20% high when the extrapolation is long. Allowing for this error, the convergence limit of the $X^2\Sigma^+$ state would be expected to lie at about $9.9 - 1.98 = 7.92$ volts. Asundi (1943), by observing perturbations in $v=7$ level of the $B^2\Sigma^+$ state, followed the vibrational levels of the $X^2\Sigma^+$ state up to $v=33$ corresponding to 55082 cm^{-1} (6.90 volts), which may be taken as a lower limit for the position of convergence of the $X^2\Sigma^+$ state.

For the states $A^2\Pi$ and $B^2\Sigma^+$, the ranges of extrapolation are comparatively shorter and consequently uncertainties lesser.

II

For CO^+ , two dissociation processes may be considered :



in which D_1 and D_2 represent the respective energies of dissociation. Let $I(\text{C})$, $I(\text{O})$ and $I(\text{CO})$ denote the the first ionization potentials C, O and CO respectively. Then the interrelations of these quantities are obtained from the following expressions :

$$\begin{aligned} \text{CO}^+(X^2\Sigma^+) + D_1(\text{CO}^+) &= \text{C}^+(^2P) + \text{O}(^3P) \\ \text{C}^+(^2P) &= \text{C}(^3P) + I(\text{C}) \\ \text{C}(^3P) + \text{O}(^3P) &= \text{CO}(X^1\Sigma^+) + D(\text{CO}) \\ \text{CO}(X^1\Sigma^+) + I(\text{CO}) &= \text{CO}^+(X^2\Sigma^+) \end{aligned}$$

Therefore,

$$D_1(\text{CO}^+) = I(\text{C}) + D(\text{CO}) - I(\text{CO}) \quad \dots \quad \dots \quad (3)$$

Similarly, $D_2(\text{CO}^+) = I(\text{O}) + D(\text{CO}) - I(\text{CO}) \quad \dots \quad \dots \quad (4)$

The known spectroscopic values of the quantities in the above expressions are :

$$\begin{aligned} I(\text{C}) &= 11.26 \text{ volts} \\ I(\text{O}) &= 13.60 \text{ volts} \\ D(\text{CO}) &= 8.87 \quad ,, \quad (\text{Sen Gupta, 1951}) \\ I(\text{CO}) &= 14.55 \quad ,, \quad (\text{Anand, 1942}) \end{aligned}$$

Substituting these values in (3) and (4) we get,

$$D_1(\text{CO}^+) = 5.58 \text{ volts} \quad \dots \quad (5)$$

$$D_2(\text{CO}^+) = 7.92 \text{ ,,} \quad \dots \quad (6)$$

Asundi and Samuel (1937) also considered the possibility of the processes (1) and (2) given, but they have a different dissociation scheme.

The limits arising out of the different combinations of the products of dissociation may now be calculated with the aid of (5) and (6) and the atomic term differences ${}^3P-{}^1D=1.26$ volts for carbon and 1.96 volts for oxygen. The results are given in Table II.

TABLE II

Products of dissociation	Calculated limits, volts	Observed limits, volts	State
C ⁺ (² P) + O(³ P)	5.58	—	—
C ⁺ (² P) + O(¹ D)	7.54	~7.33	A ² Π (?)
C(³ P) + O ⁺ (⁴ S)	9.0	(7.92)	X ² Σ ⁺
C(¹ D) + O ⁺ (⁴ S)	9.18	9.36	B ² Σ ⁺

In the last two columns the experimental results have been reproduced from Table I, but, for the X²Σ⁺ state, the estimated value 7.92 volts, has been shown instead of the extrapolated value 9.0 volts, as already discussed. The effect corresponding to 5.58 volts does not appear to have been observed so far. Thus within the limits of error in extrapolation the agreement between the calculated and the observed limits appears to be fairly satisfactory.

Gaydon and Penney (1945) have indicated the extrapolated limit of the A²Π state to be at 9.2 volts, that is, almost at the same height as that of the B²Σ⁺ state. If this value is accepted, it would mean that the effects expected at 5.58 and 7.54 volts are missing. Such a contingency is not unlikely, if we consider that the vibrational levels of the A²Π and B²Σ⁺ states have not been observed in emission beyond $v=14$ and $v=10$ respectively. The unobserved limits lie in the vicinity of the energy heights of these vibrational levels and suggest the possibility of the existence of repulsive states.

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