SPECTRAL AND COLLISION DATA OF CO^+ AND THE DISSOCIATION ENERGY OF CARBON MONOXIDE

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THAT the energy of dissociation of carbon monoxide, D (CO) cannot be much less than 10 e.v., was shown to be deducible from a number of considerations.[1] Recently, Gaydon and Penney have suggested that D (CO) lies between 9·85 and 11·11 e.v.[2] The spectrum of CO^+ corroborating the data on collision processes further offers some interesting evidence bearing on this subject.

The dissociation energy of CO is 2·9 or 0·55 e.v. more than that of CO^+ according as D (CO^+) = D (CO) + I (C) − I (CO) or D (CO^+) = D (CO) + I (O) − I (CO). The three known electronic states of CO^+ namely X $(^2\Sigma^+)$, A $(^2\Pi)$ and B $(^2\Sigma^+)$ give on linear extrapolation of the vibrational levels, energies of dissociation of 9·9, 6·0 and 3·7 e.v., and therefore dissociation limits of 9·9, 7·9 and 9·3 e.v., from the ground level of CO^+ respectively. The vibrational levels of these states are directly known upto energy values of 25,963 cm.$^{-1}$ or 3·22 e.v., 20,169 cm.$^{-1}$ or 2·5 e.v., and 14,543 cm.$^{-1}$ or 1·8 e.v., respectively.[3] Thus the extrapolation of B state is of the same order of accuracy as that of the ground state of CO. The extrapolation of A is less accurate and that of X looks comparatively long. To avoid further complications in the correlation of dissociation products the latter is generally considerably discounted.

Biskamp has observed perturbations in $v = 7$ level of B state.[4] From calculations made by us these appear to be vibrational perturbations caused by the vibrational levels of X state. Counting from the ground state of CO^+ the energy of X at $v = 33$ is 55,982 cm.$^{-1}$ or 6·9 e.v., and that of B in the seventh vibrational level is 56,330 cm.$^{-1}$ If this interpretation is correct, we practically know the levels of X upto 6·9 e.v. Its extrapolation is then of at least an equal if not greater order of accuracy than of either A and B states of CO^+ or the ground state of CO.

If to the dissociation limits of X, A and B we add I (CO) = 14·1 e.v., we get 24, 22 and 23·4 e.v., respectively. These values can be correlated

to and should be regarded as being in agreement with those obtained by collision experiments,[5] due regard being given to possible inaccuracies in both methods. Thus we identify the first two with $23{\cdot}3 \pm 0{\cdot}2$ and $20{\cdot}9 \pm 0{\cdot}2$ e.v. which are already attributed to the dissociation processes involving products $C\,(^3P) + O^+\,(^4S)$ and $C^+\,(^2P) + O\,(^3P)$ respectively. The third is identical with $22{\cdot}8 \pm 0{\cdot}2$ e.v., and represents the process in which a further excitation of O from ^3P to ^1D occurs in the second process. This is evident because the minimum spectroscopic value for the dissociation limit of B being already $1{\cdot}8 + 5{\cdot}64 = 7{\cdot}44$ e.v., it is hardly possible to correlate it with that of the A state. It must therefore involve an excited O atom $1{\cdot}93$ e.v., $(^1D - {}^3P)$, above the limit of A. Also the limit of X should be $2{\cdot}35$ e.v., $\{I\,(O) - I\,(C)\}$, above the limit of A. We thus conclude from spectral and collision data taken together that X is derived from $C\,(^3P) + O^+\,(^4S)$, A from $C^+\,(^2P) + O\,(^3P)$ and B from $C^+\,(^2P) + O\,(^1D)$.

Such a possibility has been already indicated on other grounds.[6] Atom or ion collision experiments are also interesting for this conclusion. The process $CO^+ \rightarrow C^+ + O$ is found to be particularly intense while $CO^+ \rightarrow C + O^+$ is weak and not certain.[7] This is probably due to the circumstance that in such type of collisions, processes involving comparatively large changes in internuclear distances are likely to be more favoured. This distance r_e for $X\,(^1\Sigma)$ of CO is $1{\cdot}13$ A., while r_e values for X, A* and B states of CO^+ are $1{\cdot}114$, $1{\cdot}195$—$1{\cdot}209$ and $1{\cdot}168$ A., respectively. Thus in these experiments it is A $(^2\Pi)$ which is directly reached by collision.

All these considerations show that only the extrapolation of state A is not very reliable. A glance at the values for this state deduced by various authors (namely $13{\cdot}30$ Herzberg,[8] $14{\cdot}07$ Weizel, Jevons and Sponer: Reports) confirms this suspicion. We, therefore, believe that the dissociation limits for X, A and B states deducible from spectroscopic data are $9{\cdot}9$, $7{\cdot}5$ and $9{\cdot}4$ e.v., respectively. These yield for D (CO) the values $10{\cdot}45$ e.v., from X state and $10{\cdot}4$ e.v., from A state, values which are remarkably close. From collision data on similar interpretation, we obtain $9{\cdot}2$, $6{\cdot}8$ and $8{\cdot}7$ e.v., respectively yielding for D (CO) $9{\cdot}75$ e.v., from X and $9{\cdot}7$ e.v., from A. The mean of these four values is $10{\cdot}1$ e.v.

Anand has recently reported two Rydberg series in emission in the extreme short-wave spectrum of CO and deduces $14{\cdot}5$ e.v., as their common limit.[9] If the interpretation is correct, the limit can only refer to the

* The values for the doublet state A quoted in the literature are evidently calculated on the wrong basis of regarding the (3, 0) comet-tail band as the (0, 0) band. The values quoted here are accordingly corrected.

X state of CO^+, in which case the D (CO) spectroscopic value will have to be increased by 0·4 e.v.

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