

ON THE DISSOCIATION ENERGY OF CARBON MONOXIDE.

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Received May 9, 1936.

THE energy of dissociation of the CO molecule has been the subject of a discussion since some time past. Quite recently Herzberg¹ has pointed out certain objections against the low value of 8.41 volts for $D(\text{CO})$ given by Coster and Brons². On the other hand, Schmid and Gerö³ still more recently have suggested a much lower value of 6.9 volts for $D(\text{CO})$. All these various values have been based on data of rotational pre-dissociation and we have therefore thought it desirable to point out some more objections both of an experimental and a theoretical nature.

Rotational predissociation is in general recognised by an abrupt disappearance of the individual band lines. But the converse is not always true, because such a disappearance may be brought about simply by experimental conditions, *i.e.*, by factors which have nothing to do with pre-dissociation like the intrinsic intensity of the band, the method of production depending on temperature, the sensitivity of the plate, the time of exposure etc. Indeed the predissociation at 9.66 volts above the ground level obtained by Coster and Brons and on which they very definitely based the value of 8.41 volts for $D(\text{CO})$, has been shown to be an instance of this kind. Whereas Brons did not obtain lines higher than $J = 17$ in the three bands of the fourth positive group, which he measured, Gerö⁴ obtained for the two of these bands which he measured, lines up till about $J = 34$. This significant observation not only invalidates the value of 8.41 volts for $D(\text{CO})$ but also strengthens our viewpoint that the other observations of decrease of intensity, which are ascribed to predissociation, might also arise from similar causes especially the one⁵ found in $b^3\Sigma$. Other instances of a similar kind are the Herzberg and Ångström bands in which earlier workers⁶ could only measure lines up to about $J = 25$ whereas recent work under different methods of production shows that it is possible to obtain lines with higher rotational quantum numbers. The intensity distribution especially in these bands is

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furthermore complicated and rendered chaotic by a large number of extraneous lines which Coster and Brons⁷ take for CO₂ bands, but which evidently belong to the CO bands of the system $a' \ ^3\Sigma \rightarrow a^3\Pi$. Therefore such slight irregularities cannot be called abnormal and the intensity distribution of the (0, 0) Ångström band shown in the reproduced microphotometer plate⁷, to our mind, requires further experimental confirmation on account of the numerous extraneous lines. Similar remarks apply to the decrease in intensity observed in the other Ångström band and the Herzberg bands⁸. It seems therefore doubtful, whether the dissociations at 11.54 and 11.08 volts are already definitely established.

Assuming, however, that some of these cases of intensity decrease come out to correspond to a dissociation of the molecule, the further questions arise, whether it is a case of real predissociation or the ordinary dissociation by instability of the molecule brought about by rotation. Only the former case means an improvement on the usual vibrational extrapolation. An example is furnished by S₂. The value for D (S₂) obtained from the interpretation of the abrupt termination of the rotational structure in two successive vibrational levels does not agree, as we have pointed out recently⁹ at greater length, with the value obtained from the convergence point, whatever products of dissociation are assumed for the upper electronic term. Indeed, as far as CO is concerned, it is rather surprising that most of the various predissociations would at the same time mean a violation of the selection rule in Kronig's theory of rotational predissociation¹⁰. It is sometimes assumed that such a violation is observed¹¹ in the spectrum of P₂ but even here it does not appear to be definitely established because the argument is based on the extrapolated values of the energy of dissociation of P₂ and of excitation of P which themselves are somewhat uncertain. If, however, the interpretation in the P₂ molecule is correct, it can mean only an exception to the general rule, and such exceptions can hardly be so numerous as they would be in the case of CO.

Predissociation data always give an upper limit to the energy of dissociation because they involve a certain amount of kinetic energy, which may be small or great depending upon the steepness of the repulsive curve. An exact correlation of values obtained from such data to the levels of the separated system is not to be expected and hence the existence of such exact correlation does not establish a true case of predissociation. We may illustrate it by the value of 9.66 volts of Brons, which lies 1.42 volts below 11.08, and corresponds exactly to the excitation energy of the C atom but just this value of 9.66 volts has been proved to be incorrect.

Herzberg has already pointed out¹, that the energy difference of about half a volt between the two predissociations in $C^1\Sigma$ and $B^1\Sigma$ can be explained as a true difference between terms of the separated systems only in a very artificial way and is inclined to take this amount as an excess of kinetic energy. If we assume that Kronig's selection rule is strictly valid, we shall have to explain both of these predissociations by repulsive curves originating in $C(^3P) + O(^3P)$ or $C(^1D) + O(^1D)$ (being the next higher) because only these combinations can give rise to singlet terms. In the latter case $D(CO)$ becomes 7.86 volts, a value which appears to be too low on account of thermochemical reasons, discussed later. In the former case 11.08 volts will represent $D(CO)$ plus a certain amount of kinetic energy, whose magnitude will depend on the correct value of $D(CO)$ itself. We believe $D(CO)$ to be roughly 10 volts, in which case the excess of kinetic energy would be about 1 volt. Schmid and Gerö³ report another predissociation at 9.57 in $A^1\Pi$, but details about this are not yet available and we cannot say whether our general objections against predissociation values in CO will hold good also in this case. If it is a true case, $D(CO)$ will be about 9.5 because this predissociation takes place again in a singlet level. On this view, the excess of kinetic energy for the upper one will be about one and a half volts. This rather large amount of kinetic energy can be avoided by one or other correlations, suggested by other authors, but only at the expense of the selection rule and on the assumption, except for Herzberg, that predissociation data invariably give exact values. We prefer, however, to take this excess of kinetic energy as genuine because it is obvious, that among the 18 molecular terms arising from a combination of $C(^3P) + O(^3P)$ quite a large number will be repulsive states. Since they are not degenerate and therefore possess varying slopes and since already a single one of them will intersect various electronic states at different internuclear distances according to their heights above the ground level, we do not see any difficulty in explaining this increasing excess of kinetic energy from level to level, according to the present interpretation.

From considerations of the existence of only one or two vibrational levels in the state $b^3\Sigma$, a value of $D(CO) = 10.45$ volts has been deduced¹². This will be the upper limit. If the new predissociation in $A^1\Pi$ is proved, this will be reduced to 9.57 volts. A value of this order of magnitude for $D(CO)$ is to be expected from considerations of thermochemical data on account of its intimate connection with the heat of sublimation of carbon. Herzberg has already pointed out, that the data of thermochemistry give a lower limit for $D(CO)$. We should like to add, that also the energy of the C-H bond would be reduced following a reduction in $D(CO)$ and $S(C)$.

Since free CH_3 radicals react rather rapidly with H_2 to form $\text{CH}_4 + \text{H}$ the C—H bond cannot have very much lower energy¹³ than D (H_2), which means that S (C) cannot have a much lower value than 150 Kcal/mol and D (CO) a value not much lower than 10 volts.

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