DISSOCIATION, PREDISSOCIATION, AND RECOMBINATION OF DIATOMIC MOLECULES

G. HERZBERG

As is well known, every electronic state of a molecule has a continuous range of energy-levels corresponding to dissociation or recombination of the molecule. In absorption a transition from the ground state to the continuous part of an excited electronic state, according to the Franck-Condon principle, can take place only if the equilibrium nuclear distance r_e of the upper state is appreciably larger than that of the ground state. Many examples of such continuous spectra are known. Conversely, in cases where the internuclear distances are known from emission-band spectra, one may predict with certainty whether or not a continuous absorption spectrum leading to photochemical dissociation exists. Such is the case for C_2, for which the upper state of the new $^3\Pi - {}^3\Pi$ bands[1] has such a large r_e that in absorption a continuous spectrum will appear. This is of importance for Wurm's explanation[2] of the difference in the spectra of the head and the tail of comets: the C_2 molecules present in the head are dissociated by light absorption in the continuous spectrum just mentioned, and therefore no C_2 bands appear in the spectrum of the tail.

Depending on the relative positions of the potential curves, the two atoms produced by light absorption in the continuous region may have varying amounts of kinetic energy. If one of them is excited to the upper state of an atomic line, this line appearing in fluorescence will have an anomalously large Doppler broadening.[3] This process may be of importance in explaining the large Doppler width of the coronal lines.

The converse of the photochemical dissociation of a diatomic molecule is the recombination of two atoms in a two-body collision with emission of radiation. In consequence of the short time of collision, even in case of a completely allowed electronic transition, only every 10^5 collision leads to a recombination. Yet, at pressures

[1] J. G. Fox and G. Herzberg, *Phys. Rev.*, **52**, 638, 1937.

[2] K. Wurm, *Zs. f. Ap.*, **8**, 281; **9**, 62, 1934.

[3] T. R. Hogness and J. Franck, *Zs. f. Phys.*, **44**, 26, 1927.

below 0.1 mm Hg and if collisions with the walls are not important, this recombination by two-body collision is more important than recombination by three-body collision. For some elementary molecules, such as H_2 and N_2, recombination of normal atoms can occur only by way of a forbidden transition and is therefore much less frequent.

In three-body recombinations the energy of dissociation is carried away as excitation energy by one or both of the resulting systems. An interesting example is supplied by carbon: in discharges in CO of high pressure the Swan bands of C_2 appear with only the $v' = 6$ progression (so-called high-pressure carbon bands). The selective excitation of the one vibrational level can only be understood by assuming that molecules in this state are formed directly by the recombination of two C atoms (formed by dissociation of CO) in a three-body collision, the heat of dissociation D (C_2) being transformed into energy of excitation of C_2.[4] Thus, $D(C_2) = 3.6$ volts follows.

A dissociation of a molecule can also be brought about by radiationless transition from a discrete state to one of equal energy that belongs to a continuous range of energy values. This so-called "predissociation" may be detected by the broadening of the band lines in absorption or by the breaking-off of a band system in emission at a certain value of the vibrational and rotational quantum number. For example, in the case of the new C_2 bands referred to in the first paragraph, only the $v' = 0$ progression appears. This is very probably due to predissociation of the higher levels. The predissociation limit fits well with the $D(C_2)$ value given above. Also, this predissociation of C_2 is an additional way in which this molecule may be dissociated in comets by absorption of sunlight.

An important question which, in some cases, is difficult to answer is whether the predissociation limit coincides with a dissociation limit or whether, owing to a potential maximum, predissociation sets in at a higher energy than corresponds to the dissociation limit. A decision can be reached if it can be ascertained whether the so-called "limiting-curve" of dissociation (obtained from several breaking-off points in different vibrational levels, plotted as a function of

---

[4] In the discussion Dr. Beutler pointed out that this is very probably a case of an inverted induced predissociation.