

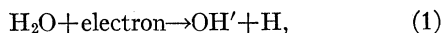
Letters to the Editor

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Abnormal Rotation in Radiative Collision of Electrons with Water Molecules

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IN order to obtain information on the mechanism of the abnormal rotation frequently observed in electrical discharges through water vapor, purely electronic impacts of water molecules have been investigated. The main purposes of this experiment are firstly to confirm the intrinsic abnormal rotation due to purely electronic collisions of water molecules, and secondly to observe its dependence on the energy of colliding electrons. It may, therefore, be necessary to observe only the collision process between water molecules and electrons with energies lying within a definite narrow range, namely,



without confusing this with other kinds of collision processes.

In order to realize such an idealized picture, a beam of water molecules is projected in the *z* direction

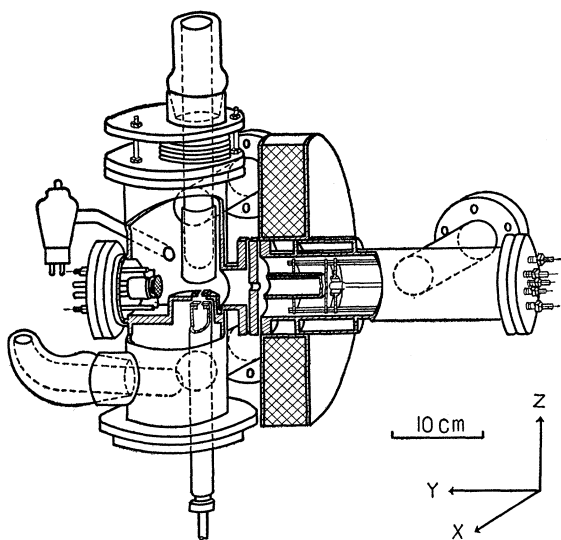


FIG. 1. The collision chamber.

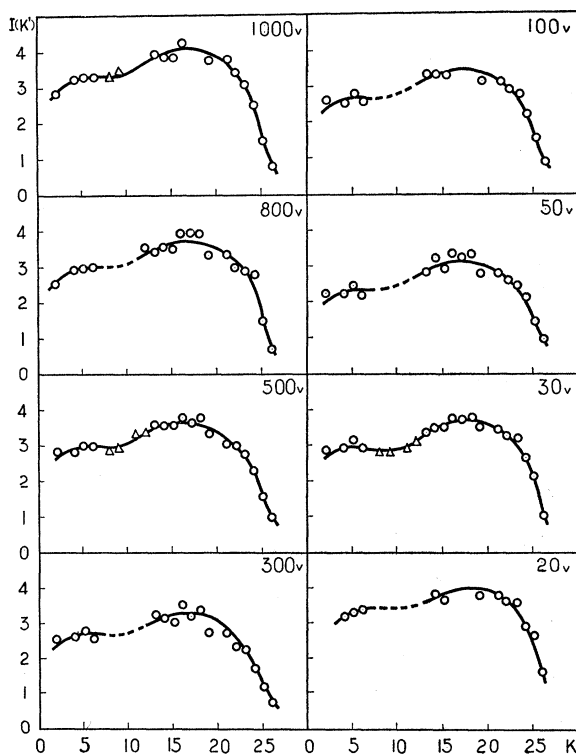
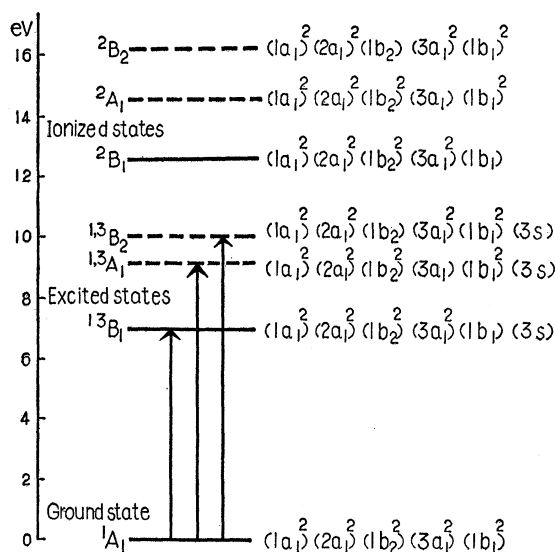


FIG. 2. Dependence of the rotational intensity distributions of the OH (0,0) band on the energy of the impinging electrons.

(see Fig. 1), and at the same time a beam of electrons with nearly uniform velocities is shot in the *y* direction. The former beam is projected into the vacuum of 1×10^{-4} mm Hg within the collision chamber through a source slit and an image slit and condensed on a metallic surface cooled by liquid air immediately after having traversed a short distance of ten millimeters or so. The latter beam is emitted from an oxide-coated cathode in a specially designed electron gun and brought to a focus just in front of the image slit by electric and magnetic means. The intensities of the rotational lines emitted in the *x* direction from the excited OH molecules appearing at the intersection of the two beams are measured by the quartz Littrow-type spectrograph with one 60° prism and one 30° prism, and a recording microphotometer with a phototube and a string electrometer. The observed rotational intensity distributions are shown in Fig. 2.

There may be involved in Fig. 2 the answers to two questions which have long remained pending, namely, what features do the abnormal rotations have owing to purely electronic collisions of water molecules, and in what manner does the energy of the impinging electrons exercise an influence upon them. The answer to the first question is that almost all of the OH' molecules are rotating abnormally. The fact that the abnormal maximum is at all times predominant over the thermal maximum stands in sharp contradiction to the situation

FIG. 3. Energy level diagram of H₂O.

in ordinary electrical discharges. The answer to the second question is that the rotational intensity distribution does not show any appreciable change in dependence on the energy of impinging electrons in the wide range from 1000 down to 20 volts or less. These characteristic features may be attributable to the nature of the excited states of H₂O taking part in the process (1).

After having been raised up to either one or both of the excited states, 1,3A_1 and 1,3B_2 as shown in Fig. 3, water molecules may be expected to dissociate spontaneously into abnormally or thermally rotating OH' molecules and recoiling H atoms. When the potential surfaces for these excited states have been evaluated, the path of the recoiling H atom will be known and at the same time the excess angular momentum accepted by the remaining H atom will also be determined by the law of angular momentum conservation.

A detailed discussion will be published in the *Journal of the Physical Society of Japan*.

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Luminescent Centers in Sulfide Phosphors

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IN recent publications^{1,2} Prener and Williams have reported that Cu⁶⁵ formed from Zn⁶⁵ by K-electron capture in a ZnS matrix is ineffective as an activator, i.e., it does not emit the green luminescence charac-

teristic of Cu in a ZnS phosphor. They state that this experiment makes the conclusion "inescapable" that an isolated copper impurity at a substitutional zinc site does not give rise to a luminescent center in zinc sulfide. Using a treatment of ZnS as a covalent solid, they propose an explanation based on the absence of coactivator centers in this experiment; and finally they suggest that a luminescent center requires the activator and coactivator to occupy second or third nearest-neighbor positions to each other.

It is the purpose of this letter to point out that the above-mentioned conclusion is not inescapable, and that the experimental result of Prener and Williams can be understood on the basis of a current well-known model of sulfide phosphors³ which treats them as primarily ionic structures. On the ionic model, the copper ion responsible for the green luminescence in ZnS is Cu⁺¹. If Cu⁶⁵, formed by decay of Zn⁶⁵ in the Prener and Williams experiment, is built into the ZnS crystal as Cu⁺² ion, as one would expect, its ineffectiveness as an activator is readily understood without additional complications. Thus on the ionic picture the copper ion produced in this experiment is not of the correct charge to constitute a luminescent center; it would not be directly excited by the 3650 Å light. The only possibility for luminescence would then be by charge transport processes. Prener and Williams argue that such processes occur by analogy with the results of a theoretical treatment of superlinear luminescence in ZnCdS:Ag, Ni.⁴ There appears, however, to be no direct experimental evidence to indicate that the high probability of ionization holds for all 3650 Å excited centers in ZnS:Cu. If these centers are not thermally ionized, then the Cu⁺² centers formed by radioactive decay should not change the luminescent intensity. If the centers are thermally ionized then the relative amount of green luminescence might increase. In order to determine whether there should be a significant increase or not it would be necessary to know the concentrations of all centers involved, detailed models of electron and hole motion leading to luminescence, and cross sections for capture of the charge carriers by the various centers. These quantities are in general not known.

It appears therefore that the experiment can be understood either on the basis of the conventional ionic model or on an interpretation of ZnS as a covalent material. Furthermore, the experiment does not necessitate a revision of the usual viewpoint that isolated activators can luminesce.

We are indebted to Dr. Prener and Dr. Williams for communications on this subject.

¹ J. S. Prener and F. E. Williams, *Phys. Rev.* **101**, 1427 (1956).

² J. S. Prener and F. E. Williams, *J. Electrochem. Soc.* **103**, 342 (1956).

³ H. A. Klasens, *J. Electrochem. Soc.* **100**, 72 (1953).

⁴ S. Roberts and F. E. Williams, *J. Opt. Soc. Am.* **40**, 516 (1950).