Molecular Spectra of the Alkali Hydrides

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AN ABSTRACT

Work on the spectra of the alkali hydrides was begun in 1927 by Johnson who published a brief report on NaH, but it was not until 1930 that intensive study of these molecules began. In that year Nakamura published an extensive report on the absorption and emmission spectra of LiH, and this was quickly followed by investigations in absorption and emmission on NaH and KH by Hori, and Almy and Hause respectively. Since that time all of these have been re-investigated and the work greatly extended. Lithium deuteride and sodium deuteride have also been done, and by study of the isotope effect the uncertainties in the v′ numbering in the excited states of these two molecules have been cleared up. In the spring of the present year the author has succeeded in photographing the absorption spectrum of CsH, and is now in the midst of work on that of RbH. All the alkali hydride spectra so far reported are due to $^2\Sigma$ — $^2\Sigma$ transitions and are of the many line type showing no heads or regularities of any kind on casual inspection. This is due to the great overlapping of the bands, and to the fact that the heads are very close to the origins around which the intensity of the lines is very low.

These alkali molecules are of particular interest as a group on account of some very unusual anomalies which characterize their excited states, and have not been found elsewhere. Before going into the details of these peculiarities, however, it is necessary to say something of the experimental technique and methods of excitation.

Crystalline alkali hydrides are fairly easily formed by heating the metallic alkali in an atmosphere of dry hydrogen to temperatures ranging from about 300°C for NaH to about 600°C for CsH. In practice, however, this apparently simple procedure is greatly complicated by the active nature of the alkali metals, their violent reaction in the presence of moisture, and the rapidity with which they darken glass at even moderate temperatures. The hydrides are even more active than the metals, which makes it necessary to form the compound in the absorption tube itself which must then be of steel or nickel and not of glass. This immediately leads to wax seals at the ends which have to be water cooled. The resulting non-equilibrium condition of the vapor in the tube allows a rapid condensation of the hydride at the cool ends where it gathers in large cotton-like masses which soon choke up the tube.

For the work on CsH a heavy walled steel tube 140 cms long was used. It was provided with a taper grease joint at one end through which a boat containing the metallic caesium under carefully dried xylol was introduced and pushed to the center of the heated section. This was carried out under flowing dry nitrogen, which was pumped off with the xylol. Hydrogen was then introduced through a drying train. The tube was heated with electrical

units so designed as to provide a higher temperature at the ends than at the center of the heated section in order to retard the diffusion of the vapor to the water jackets. Although this helped somewhat, the exposure time was limited to about 30 minutes at the end of which the deposit closed the tube.

For emmission the method is to introduce the alkali metal into a water-cooled d.c. arc burning in an atmosphere of dry hydrogen. This is accomplished by drilling the lower electrode and fitting it with a plunger controlled from outside so that the metal may be introduced a little at a time into the arc.

The energy of any level in a diatomic molecule in a $^1\Sigma$ state may be expressed as the sum in three parts, T^e contributed by the electronic configurations of the electrons in the atoms, G(v) due to the vibrations of the atoms, along the internuclear axis, and F(K) due to the rotation of the molecule about the common center of mass. This may be more completely expressed in the following expression:

$$E = T^e + \omega_e (v + \tfrac{1}{2}) + x_e \omega_e (v + \tfrac{1}{2})^2 + y_e \omega_e (v + \tfrac{1}{2})^3 + \ldots . + B_v K(K + 1) + D_v K^2(K + 1)^2 + F_v K^3(K + 1)^3 + \ldots . \quad (1)$$

in which ω_e is the frequency of infinitesimal vibration about equilibrium, $x_e\omega e$ (usually positive) accounts for the anharmonicity, B_v is inversely proportional to the moment of enertia of the molecule, and D_v accounts for the stretching of the molecule under central forces. B_v depends upon v according to the relation

$$B_v = B_e - \alpha_e (v + \tfrac{1}{2}) + \gamma_e (v + \tfrac{1}{2})^2 + \ldots \ldots \quad (2)$$

in which B_e is the extrapolated value of B_v and is equal to $\frac{h}{8\pi^2 c I_e}$, I_e being the moment in inertia of the non-vibrating molecule. α_e is usually a positive quantity.

In general the vibrational levels are quite accurately expressed by the first two terms in the vibrational quantum number v, and B_v by the first two terms of (2). This is also true for the ground states of the alkali hydrides, but in the excited states this is far from correct. Fifth degree polynomials are necessary in both cases even for fairly low quantum numbers as the curves representing $\Delta G(v + \tfrac{1}{2}) = G(v + 1) - G(v)$ plotted against v, and B_v plotted against v both fall off steeply for values of v less than 6 or 7. This would seem to indicate in the latter case that the molecule expands as it shrinks since the moment of inertia suddenly starts to increase as the vibrations become smaller and smaller.

This peculiar behavior has been explained on the basis of a sort of rotational uncoupling, but this theory which never did explain the anomaly in the vibrational levels, has lost most of its support with more complete knowledge of the hydride spectra.