Fluorescence of the KH molecule*

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Previously, the potassium hydride molecule, like other alkali hydrides, has only been observed[1–3] in absorption and in emission. We report here the first study of KH fluorescence, excited by both a pulsed tunable dye laser and by the lines of a cw argon ion laser. With the ability to excite fluorescence in this class of molecules, one can look forward to obtaining increasingly refined structural information on the excited state (such as the variation in dipole moment as a function of vibrational level) through fluorescence interference techniques,[4] in addition to observing higher vibrational levels of the ground state than have ever been seen. Moreover, the fluorescence of alkali hydrides opens the possibility of their detection as products in a reactive molecular-beam scattering experiment.[5]

Potassium hydride was generated by heating lump potassium in a 2 in. diameter cross-shaped oven (450–600 °C) filled with H_2 gas (100–700 torr). The windows were water-cooled and condensation rings formed in these regions, ultimately blocking the light path (3 h operating time). No darkening of the windows occurred during this period.

The only electronic transition observed in KH is the visible $A\,^1\Sigma^+ - X\,^1\Sigma^+$ system, which is a many-lined spectrum with no band heads. Using the 4880 Å line of the argon laser, fluorescence was excited in the $A-X$ system corresponding to the transition $(v''=0,\ J''=5) \rightarrow (v'=7,\ J'=6)$. The fluorescence was viewed at right angles to the laser beam by a $\frac{3}{4}$-m SPEX spectrometer with an S-20 photocathode. The large spacing between P and R doublets for this hydride system permits easy identification of the (v', J') vibrational-rotational level excited, using the previous line position measurements of Almy *et al.*[1] and Hori[2] combined with the corrected vibrational numbering of Bartky.[3] The (7, 0), (7, 1), (7, 2), and (7, 4) P and R doublets were observed. Intense K_2 absorption ($B-X$ system) in the oven limited observation of the KH fluorescence further to the red. The 4965 Å laser line appeared to give very weak fluorescence, while the other lines seemed not to excite KH. In an attempt to observe KD fluorescence H_2 was replaced by D_2 but none of the argon ion laser lines was found to be effective.

A nitrogen-laser-pumped dye laser was also used to excite KH fluorescence in the regions 4400–4700 Å (dye: 7-diethylamino-4-methylcoumarin) and 4800–4930 Å (dye: 3-aminophthalimide). The excitation spectrum was observed in the same manner as described previously[5]: optical filters were used to exclude scattered laser light. As the dye laser, with a bandwidth of about 0.5 Å, was tuned to the $(v', 0)$ lines previously observed in emission, the expected fluorescence signal was obtained. A portion of the excitation spectrum is illustrated in Fig. 1.

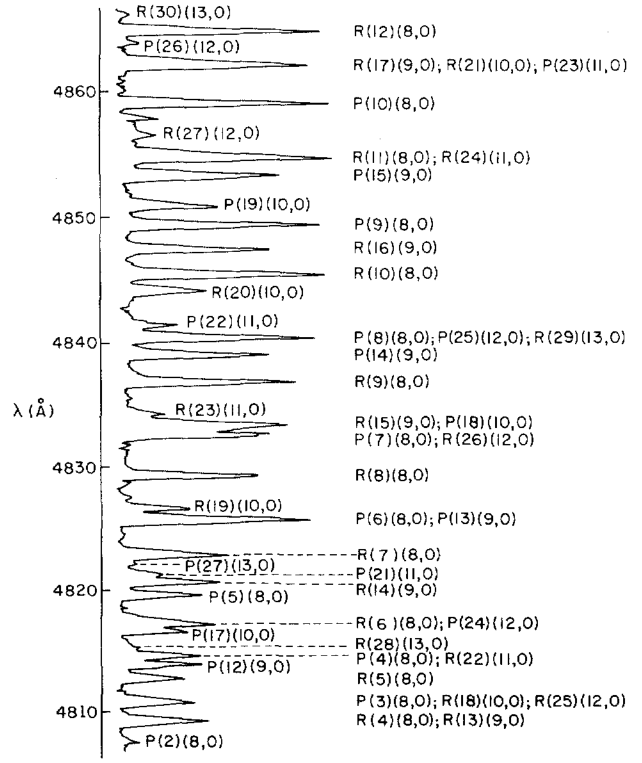

FIG. 1. Portion of the KH excitation spectrum taken with a dye laser having about 0.5 Å bandwidth. The assignments are based on emission line positions taken from the literature.[1–3] (No correction is made for variation in laser intensity with wavelength.)

The dye laser has a pulse width of about 5 nsec and the response time of the detection electronics is of similar magnitude. Direct observation of the radiative decay of KH as a function of time enables us to estimate the lifetime of KH* under our operating conditions. Over the range of hydrogen pressure available, the rate of decay of KH* was always faster than the detector response. These observations suggest that the radiative lifetime of the KH $A\,^1\Sigma^+$ state is less than 10 nsec. This conclusion, namely that the A state of KH has so short a lifetime, is not surprising in view of the transition dipole moment calculations of Docken and Hinze[6] for the analogous $A-X$ system of LiH.

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