

Laser-Induced Fluorescence and Inelastic Collisions of KH Molecule

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The laser-induced fluorescence spectrum of KH vapor, excited by the 4881-Å argon ion laser line, was obtained and analyzed. The transition was found to involve the $A^1\Sigma^+$ and $X^1\Sigma^+$ states. Vibrational and rotational energy transfer is detected. The spectrum presents a clear differentiation of bandheads. The molecular constants obtained are in good agreement with the previously reported data.

INTRODUCTION

The spectroscopic study of alkali hydrides so far has been a matter of controversy and argument, because we are dealing with spectra of many lines without well-defined bands. The results reported here refer to the KH molecule. The need for a rotational study has been pointed out in earlier papers (1-2). Indeed, Bartky's research shows that in earlier papers there have been errors in the determination of v' and J' of the state $A^1\Sigma^+$ (3-4).

KH has been studied both in absorption and emission. More useful information has been obtained for emission in KH because for absorption a great deal of interference from the K_2 molecule occurs. With the development of lasers, the possibilities of spectroscopy have been enhanced and, regarding the analysis of the KH spectrum, Zare's work (5) with an Ar^+ laser has been outstanding. In this paper, he suggests the possibility of exciting the KH transition $A^1\Sigma^+ \leftarrow X^1\Sigma^+(v' = 7, J' = 6; v'' = 0, J'' = 5)$, with a laser beam of 4881 Å.

In Zare's study the detected fluorescence spectrum consisted of doublets corresponding to $v'' = 0, 1, 2$, and 4. Recently, Giroud (6) has used a pulsed dye laser and observed the fluorescence doublets that correspond to five excitation transitions.

In the present paper we analyze the fluorescence spectrum induced by an Ar^+ laser beam of 4881 Å. We have detected in this spectrum the fluorescence doublets that correspond to the excitation transition mentioned above. The doublets observed are for $v'' = 0, 1, 2, 3, 4$, and 5. Also the complete rotational structure appears clearly in the 7-0, 7-1, and 7-2 bands. The 7-3 and 7-4 bands are partially developed and in 7-5 we could only observe the fluorescence doublet. We also observed parts of the 8-0, 8-1, 6-0, 6-1, 6-2, and 6-5 bands.

EXPERIMENTAL DETAILS

In order to produce KH, we used a cell furnace with cooled windows connected to a vacuum system. The temperature in the cell was measured by a thermocouple.

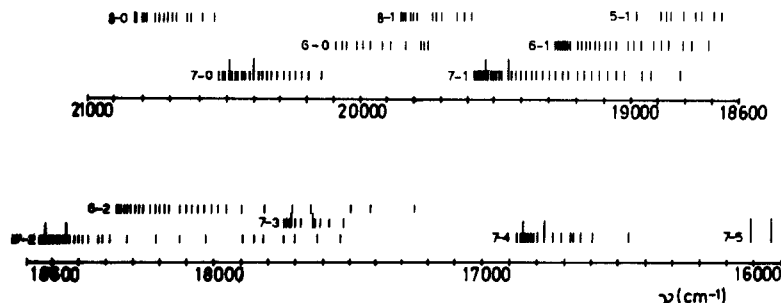


FIG. 1. Schematic representation of observed KH bands. $A^1\Sigma^+ \rightarrow X^1\Sigma^+$ system.

The experimental layout is similar to that described in earlier papers (7-8). Potassium was placed in the cell and subjected to slight heating under vacuum for 1 hr. Afterwards hydrogen was introduced at a pressure of 10-20 mm Hg. The cell was kept at a temperature of 700° K. Under these conditions, it was excited with an Ar^+ (cw) laser beam of 4881 Å and high fluorescence was obtained. The spectrum could be recorded for 1-2 hours depending on the quantity of potassium used, since it becomes deposited on the cooled parts of the cell with lapse of time.

The fluorescence is focused on the slit of a moderate resolution spectrograph which has an average dispersion of 6 Å/mm in the region of interest. The spectrum is recorded on a Kodak 103F plate. In order to calibrate the spectrum we made use of the ArII lines.

We used a precision commercial comparator to measure the spectral line positions. The line positions were measured several times and we found that the measurements could be repeated with an average variation of less than 5 μm. After measuring the position of the ArII lines and KH fluorescence lines, the dispersion of the plate was determined from the ArII calibration lines in order to compute the wavelengths of the KH lines. For this purpose a computer program was used. It describes the dispersion by a hyperbolic function and the coefficients are determined by a least-squares fit. In order to estimate the intensities of the KH lines we used a microdensitometer.

With assignments of the distinct fluorescence frequencies associated with given v' , J' , v'' , and J'' , a least-squares fit was made to obtain the molecular constants. The programs mentioned above were developed in APL language and for our calculations we used an IBM 370 computer.

EXPERIMENTAL RESULTS AND DISCUSSION

The analysis of the excitation of KH using Ar^+ laser beams demonstrated that KH fluorescence could only be obtained with the 4881-Å line. This information already had been obtained (5). However, the spectrum that we observed is more complex than the ones observed previously since the earlier workers only referred to fluorescence doublets. A reproduction of the spectrum is shown in Fig. 1. As can be seen from Fig. 1, apart from the fluorescence doublets corresponding to the level excited by laser radiation ($v' = 7$, $J' = 6$ and the ground-state vibrational levels $v'' = 0, 1, 2, 3, 4$, and 5, indicated by larger pencil strokes) we can also see satellite lines of lower

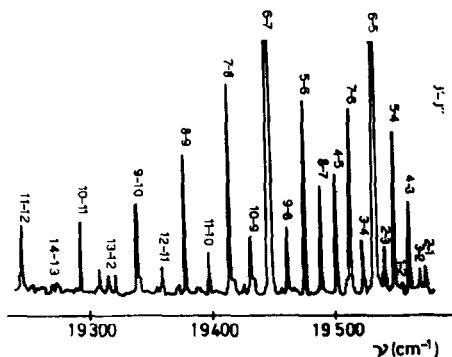


FIG. 2. Densitometer trace of the 7-1 band.

intensity which give rise to an emission spectrum from the level $v' = 7$ to $v'' = 0, 1, 2, 3$, and 4. At $v'' = 5$ only the fluorescence doublet appears.

These data can be interpreted as being due to the population changes of the rotational levels $v' = 7$ from $J' = 0$ to $J' = 20$ and even higher. These population changes are induced by collision mechanisms.

In the spectrum in Fig. 1 the 8-0, 8-1, 6-0, 6-1, 6-2, and 5-1 bands can be distinguished. These bands can be interpreted as being due to the population of the rotational levels of vibrational states having $v' = 8, 6$, and 5 with the loss or gain of vibrational energy through collisions.

A densitometer trace of the 7-1 band (which is the sharpest one), was made in order to study the effect of collisions on the loss or gain of rotational energy. This trace is shown in Fig. 2. It shows perfectly the lines of the *P* and *R* branches for the lowest rotational levels and also how the *P*(1) and *R*(0) lines do not appear due to their low intensity.

The plot of the logarithm of $I_{em}/J' + J'' + 1$ versus $J'(J' + 1)$ for each of the branches (except the fluorescence doublet) is shown in Fig. 3 in order to see the relationship of the intensities of the lines appearing due to collisions. From this figure it may be noted that the population of the states does not correspond to thermal equilibrium, since in this case a straight line would be expected for each of the branches in accordance with the expression (9, p. 205)

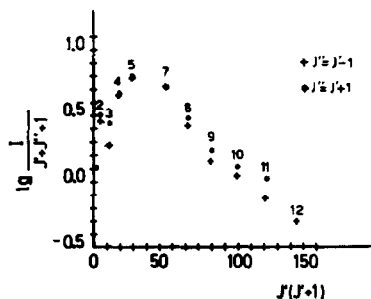


FIG. 3. Intensity distribution of the 7-1 band (intensity: rel. units).

$$\log \frac{I_{\text{em}}}{J' + J'' + 1} = A - \frac{B_v J'(J' + 1)hc}{KT}. \quad (1)$$

The intensities in the *P* branch are slightly higher than those in the *R* branch (9, p. 126), which agrees with the expression

$$I_{\text{em}} \propto \nu^4 (J' + J'' + 1) e^{-B_v J'(J' + 1)hc/KT} \quad (2)$$

since the points represented have the same J' value and have $J'' = J' + 1$ for the *P* branch and $J'' = J' - 1$ for the *R* branch.

We can also see in Fig. 3 the different behavior for the intensity variation in both sides of the excited levels. Thus the behavior of the intensity variations is different for values of J' less than six than for higher values. This is interpreted as being due to the fact that there is a limit $J' = 0$ for the loss of rotational energy by collision whereas no limit exists for the gain of energy by collision. It is also interesting to emphasize the minimum of intensity which exists for $J' = 3$.

This argument sounds reasonable given the pressure used in the experiment and taking account of the previous interpretations given in the bibliography (10). The variations in rotational energy are fundamentally due to the consecutive collisions from $J' = 6$ to different J' values. It can be seen that with reference to collisions with variations in vibrational energy, the J' values for the bands 8-0, 8-1, 6-0, 6-1, 6-2, and 5-1 are near to, and include, $J' = 6$. This clearly indicates that collision in these cases is with variation in vibrational energy while the rotational angular momentum does not vary noticeably. Similar conclusions have been expressed in other papers studying collisions of Na_2 with He (10).

Once all the lines observed had been obtained, we proceeded to calculate the molecular constants of the ground state. First, this was done only with the lines corresponding to the bands 7-0, 7-1, 7-2, 7-3, 7-4, and 7-5 and then including the bands with vibrational collisions. The constants obtained along with their typical errors are given in Table I. We also present for comparison results of previous works (2, 6). Using a simplified RKR method (11) we obtained the classic turning points for the first six vibrational levels of the state $X^1\Sigma^+$. We do not include the constants for the state $A^1\Sigma^+$ as we do not have much information for the vibrational levels of the *A* state. However, the anomalous behavior of the vibrational spacing of the *A* state is evident. Thus the vibrational energies for the *A* state when applied to $v'' = 0$, $J'' = 0$ of the *X* state are $v' = 5$, 19 964.88; $v' = 6$, 20 244.50; $v' = 7$, 20 528.19; $v' = 8$, 20 815.96. The $\Delta G'(v' + 1/2)$ values are 279.60, 283.69 and 287.77. (All the constants mentioned here are in units of cm^{-1}).

CONCLUSION

The most important part of the present paper is that it demonstrates quite clearly the structure of the transition spectrum $A^1\Sigma^+ \rightarrow X^1\Sigma^+$ of KH. This molecule has an absorption and emission spectrum of many lines without well-defined bands. However, the fluorescence spectrum induced by laser beams, which correspond to a sole radiative transition in conjunction with inelastic collisions with variations in vibrational or rotational energy, presents a clear differentiation of bands and bandheads.

TABLE I
Molecular Constants and Classic Turning Points for $X^1\Sigma^+$ KH State

| | A | B | C | D |
|------------------|----------------------|----------------------|--------------------|--------|
| ω_e | 986.482 (0.380) * | 986.595 (0.392) | 983.63 (0.57) | 985.38 |
| $\omega_e x_e$ | 15.4844 (0.1673) | 15.4628 (0.1807) | 14.32 (0.10) | 15.08 |
| $\omega_e y_e$ | 0.1206 (0.0211) | 0.1139 (0.0235) | --- | 0.1 |
| B_e | 3.4122 (0.0044) | 3.4087 (0.0042) | 3.4123 (0.0013) | 3.415 |
| α_e | 0.08247 (0.00044) | 0.08279 (0.00046) | 0.0817 (0.0010) | 0.081 |
| $D_e \cdot 10^4$ | 1.563 (0.068) | 1.474 (0.069) | 1.5 | 1.63 |

A : With the data of bands 7-0, 7-1, 7-2, 7-3, 7-4 and 7-5.

B : With the data A more other bands detected.

C : Ref. (2).

D : Ref. (6).

| v'' | 0 | 1 | 2 | 3 | 4 | 5 |
|-------------|--------|--------|--------|--------|--------|--------|
| $r_{\max.}$ | 2.4472 | 2.6234 | 2.7605 | 2.8827 | 2.9973 | 3.1073 |
| $r_{\min.}$ | 2.0717 | 1.9645 | 1.8985 | 1.8492 | 1.8097 | 1.7768 |

* Typical error.

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