The intensity behaviour of the laser-induced fluorescence spectrum in the KH molecule*

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Abstract—Collisional processes involving changes in rotational and vibrational quantum numbers are detected in laser induced fluorescence spectrum of KH molecule.

The knowledge of the Franck–Condon factors in the involved transitions allows us to evaluate a relative variation of R_e^2 versus the v'' vibrational quantum number. In the same context a population analysis was made for the $v' = 7$ vibrational level.

INTRODUCTION

The intensity spectroscopic studies are generally difficult because there are some theoretical aspects which must be taken into account. In alkali hydride molecules, the anomalous behaviour of the excited $A^1\Sigma^+$ state adds a greater difficulty due to the problems in obtaining potential energy curves.

The KH $A^1\Sigma^+$----$X^1\Sigma^+$ electronic transition has been the subject of a number of studies starting with the arc discharge emission work of ALMY and HAUSE [1–6]. Recently, GIROUD and NODELEC [7] have carried out time resolved fluorescence studies of KH in a microwave discharge and in this way measured the A state vibronic lifetime as well as vibrational and rotational energy transfer with H_2 and plasma electron.

In this paper we wish to present a study of the intensity behaviour in a laser induced fluorescence spectrum, comparing the observed values and the calculated Franck–Condon factors. In the course of this study, observations about collisions with H_2 and population distribution have been made. Moreover an R_e^2 variation as a function of vibrational quantum numbers is observed for the ground state.

EXPERIMENTAL

The experimental set up has been described in previous papers [4–5]. To produce KH, we used a cell-furnace with refrigerated windows connected to a vacuum system and temperature control. Potassium was placed in the cell and subjected to vacuum extraction and slight heating. Hydrogen was introduced at 10–20 torr. The cell was kept at 700°K.

488.1 nm Ar ion laser line is used for excitation. The fluorescence is focused on the slit of a moderate resolution spectrograph with an average dispersion of 6 Å/mm.

An enlarger with a micrometric screw and digital micron expression was used to measure the spectra. The line intensities were measured in a Joice densitometer and the area under the line shape is assumed their intensity.

Two hundred lines in the 20000–16000 cm zone were

measured. These lines correspond to only six direct fluorescence doublets and to a large number of satellite lines induced by a collisional process with change in rotational and vibrational energy [4]. Figure 1 shows the 7-1 band densitometric trace in the spectrum and Fig. 2 show the relative intensity of the fluorescence doublets.

Franck–Condon factors calculation

In order to obtain the Franck–Condon factors, potential energy curves of $A^1\Sigma^+$ and $X^1\Sigma^+$ electronic states are necessary. These curves are obtained by a modified RKR method developed in our laboratory [8]. This method assumes a mixed potential composed by a Huffaker potential in the minimum zone, an RKR potential in the intermediate zone and a van der Waals potential in the zone close to the dissociation limit. The classical turning points obtained by this method are similar to those reported by STWALLEY et al. [6].

The Franck–Condon factors have been evaluated by using wavefunctions obtained from a Morse potential distorted to reproduce the RKR turning points of the involved states in the transitions. This method is very simple and the results obtained are in good agreement with the ones obtained by other more complicated procedures [9].

In Table 1, Franck–Condon factors for observed transition are shown, so that, classical turning points and energy values used in our calculations are presented. All calculations were made using an IBM/4341 system.

RESULTS

Table 2 shows the observed values for intensity of doublets compared with the calculated Franck–Condon factors. Intensity values are normalized to the highest value.

Assuming that [10]

$$I_{em} = N_v, v^4 K R_{nm}^2 \tag{1}$$

$$K = 64/3\pi^4 c \tag{2}$$

and

$$R_{nm}^2 = \bar{R}_e^2 |\int \psi_v' \psi_v'' dr|^2 |\int \sin\theta\cos\theta\,\psi_r'\psi_r''\,d\theta\,d\psi|^2 \tag{3}$$

it is possible to evaluate R_e^2 for all v'' values because the first integral in Eqn (3) is the known Franck–Condon factor and N_v, K and the second integral in Eqn (3) are constants for the intensity of doublets.

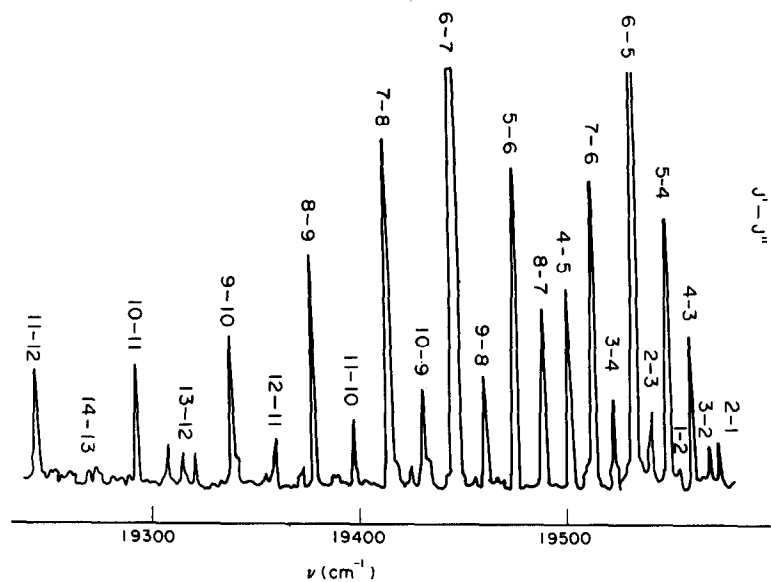The obtained values R_e^2 are shown in Fig. 3. This

Fig. 1. Densitometric trace of the 7-1 band in the spectrum.

Table 1.

v	Potential for $A^1 \Sigma^+$ state			v	Potential for $X^1 \Sigma^+$ *state*		
	$G_v + Y_{00}$ (cm^{-1})	r_+ (Å)	r_- (Å)		$G_v + Y_{00}$ (cm^{-1})	r_+ (Å)	r_- (Å)
5	1396.7051	4.9237	2.5582	0	489.1204	2.4470	2.0714
6	1676.1033	5.0301	2.4827	1	1444.8123	2.6229	1.9636
7	1969.3411	5.1334	2.4183	2	2371.4685	2.7593	1.8975
8	2248.1597	5.2350	2.3624	3	3269.6196	2.8808	1.8478
				4	4139.7891	2.9945	1.8076

Franck–Condon factors for observed A–X transitions $\times 10^3$

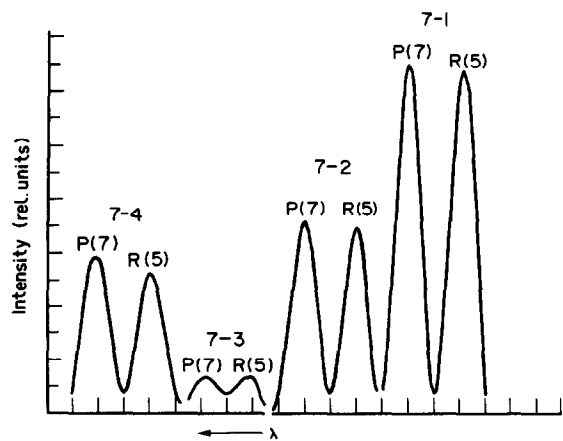| $v'' \backslash v'$	5	6	7	8
0	26.6	53.6	91.0	133.0
1	68.1	95.4	102.0	79.2
2	94.4	81.3	40.4	5.1
3	66.8	19.8	0.3	25.0
4	13.9	3.3	36.9	50.6

Fig. 2. Relative intensity of fluorescence doublets.
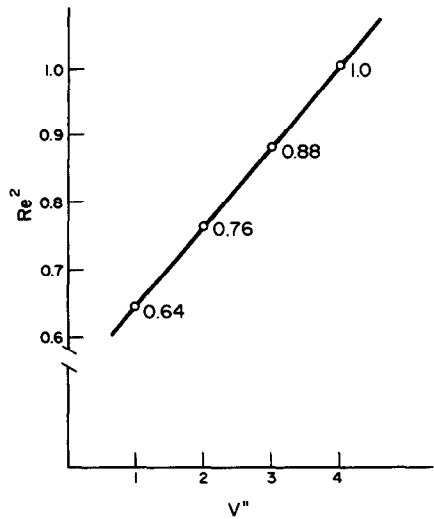
Fig. 3. R_e variation with v'' quantum number value

Table 2.

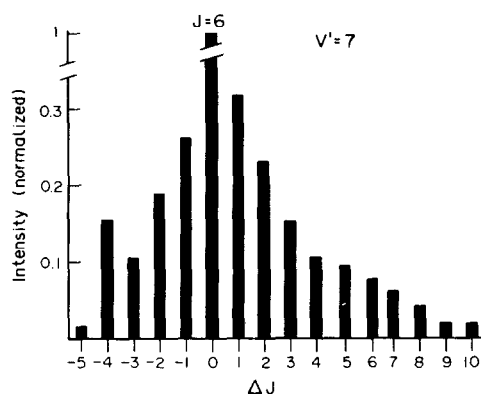| Transition		Fluorescence doublets intensity				
v'	v''	I_P	I_R	$I_P + I_R$	$FCF \times 10^3$	$I_P + I_R$ (normalized)
7	1	65.55	64.83	130.38	102.04	102.04
7	2	25.07	24.50	49.57	39.86	38.79
7	3	0.21	0.20	0.41	0.35	0.32
7	4	20.68	20.47	41.15	37.41	32.20

Fig. 4. Relative population of adjacent rotational levels in 7-1 band of the spectrum.

figure shows a linear variation of R_e^2 with v'' values in the zone of observed transitions.

Similar considerations permit one to obtain relative population in adjacent rotational levels, which are populated by collisions. The relative population in rotational levels close to the directly excited rotational level appears in Fig. 4. The behaviour of these populations are similar to the other alkali hydrides [11].

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