

RESEARCH ARTICLE | OCTOBER 15 1982

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J. Chem. Phys. 77, 3998–4005 (1982)

<https://doi.org/10.1063/1.444363>



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Lifetimes and collisions in KH, $A^1\Sigma^+$, $v'=5-22$

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(Received 24 May 1982; accepted 2 July 1982)

KH obtained in a high frequency discharge in $K + H_2$ is selectively excited by a pulsed dye laser to $A^1\Sigma^+$, $v'=5-22$, $J'=8$ or 9 . The radiative lifetimes are measured. They decrease slowly from $v'=5$ (64 ns) to $v'=19$ (53 ns) and rapidly at $v'=22$ (34 ns). Rotational transfer cross sections by collisions with H_2 increase from $v'=5$ (41 Å²) to $v'=19$ (92 Å²) as do the electric dipole moments in the levels. The collision with the electrons of the discharge provide rotational transfers where the $\Delta J' = \pm 1$ transitions are the greatest and vibrational transfers $\Delta v' = \pm 1, \pm 2$, where the $\Delta J' = 0$ transitions are small. These results are to be expected in polar molecules where the interaction of the electron with the permanent dipole moment of the molecule is predominant.

I. INTRODUCTION

The alkaline hydrides ($A^1\Sigma^+ - X^1\Sigma^+$) transition has been studied long ago by conventional spectroscopy and is now studied by dye laser excitation. The $A^1\Sigma^+$ radiative lifetime has been measured for a few v' states in LiH^{1,2} and NaH.^{1,3} In LiH these radiative lifetimes have been calculated for all the v' levels.⁴ They show a maximum for intermediate v' values and tend to the metal lifetime at the dissociation limit.

In these molecules due to the relative location of the $X^1\Sigma^+$ and $A^1\Sigma^+$ potential curves it is possible to excite many $A^1\Sigma^+$ v' states from the $X^1\Sigma^+$ $v''=0$ or 1 states which are the most populated. We have measured the lifetimes τ in a series of $A^1\Sigma^+$ v' states as completely as possible in order to look for an eventual variation of τ with v' . We have chosen KH as it is relatively easy to be produced in a discharge and to be excited by visible light obtained with common pulsed lasers.

In the course of these experiments, observations about collisions with H_2 and with the electrons have been made: quenching and rotational excitation transfers with H_2 , rotational and vibrational excitation transfers with the electrons.

II. EXPERIMENT

The apparatus is very similar to which has previously been used in our laboratory to study other hydrides⁵ and especially NaH.³

A piece of about 2 cm³ of distilled potassium is placed in the cell (Fig. 1). The hydrogen pressure varies from 5×10^{-2} to 1 Torr. High frequency (2240 MHz) electric power provided by a 200 W magnetron is applied on the cell. Such a powerful discharge is necessary to produce the hydride. The laser excitation and the observation are made through windows carried by perpendicular tubes heated to prevent depositions of the metal. In these conditions the cell may be operated for about 30 h after which all the K has crossed the observation region and the cell has to be cleaned with water and refilled.

We use an AVCO C 5000 A N_2 laser at 200 Hz to pump a dye laser made in our laboratory which provides 0.2 Å linewidth. The alkaline hydrides present a "many lines"

spectrum due to the overlap of the vibrational bands, and care has to be taken to ensure the identity of the excited level. The laser wavelength is measured within 0.2 Å with a THR JOBIN-YVON monochromator. A fluorescence spectra is recorded to verify that the excitation is selective. The excited rotational level is chosen among the most populated at the temperature of the experiment, the one of $J'=8$ or 9 which may be selectively excited. The v' levels and the line excitations (R or P) are chosen according to the optimum wavelengths provided by the dyes. The KH line wavelengths are found in conventional spectroscopy spectra⁶ or calculated from molecular constants.^{7,8}

The photomultiplier is a fast focused 3 ns time spread high gain EMI 9816. The fluorescence is sampled by a PAR 162/163 boxcar with 1 ns gatewidth. The time base has been calibrated against a radio frequency synthesizer HF period. A few 100 s runs, i.e., exponential decay curves, are averaged for each pressure and about six points are used to extrapolate the lifetime with the H_2 pressure. The fluorescence may also be integrated with a Brookdeal boxcar with 500 ns gatewidth much greater than the lifetime, to record a spectra the monochromator wavelength varying with time.

III. PRELIMINARY OBSERVATIONS

Preliminary lifetime measurements have given no reproducible results and shown the necessity to discuss the experimental conditions. The high frequency discharge provides both the vaporization of the metal and

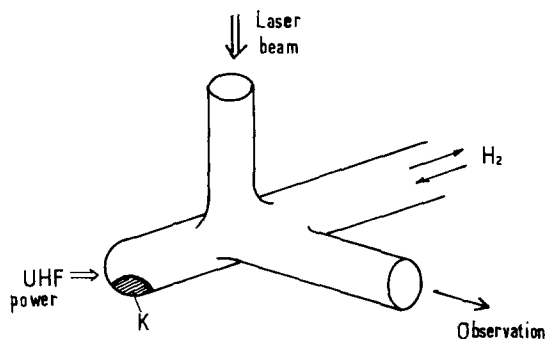


FIG. 1. The cell.

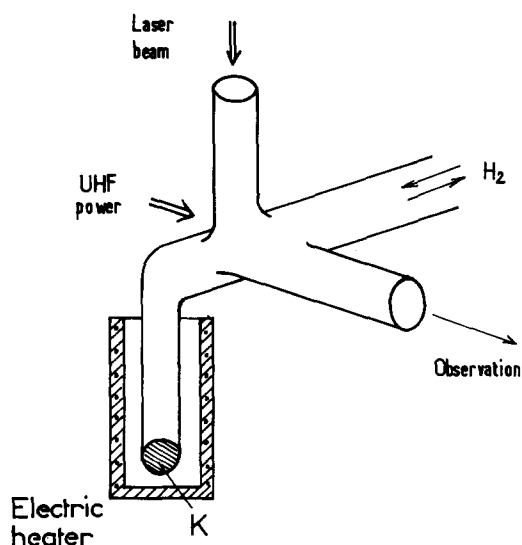


FIG. 2. A modified cell used in a preliminary experiment to separate the effects of the K pressure and of the electrons.

the electronic excitation necessary for the synthesis of the hydride. To look for the influence of these two effects, we have modified the experimental arrangement: the metal is placed in a tail heated in an electric oven (Fig. 2); the electric power is applied near the observation region so as the discharge does not reach the metal in the tail.

Lifetime measurements have been made at a given H_2 pressure, with a given electric power, but varying the

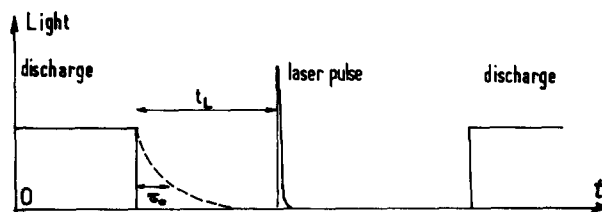


FIG. 3. The laser pulse delay t_L in the discharge cutoff.

temperature of the tail from 118 to 350°C which provides metal vapor pressures varying from 10^{-4} to 1.4 Torr. When this pressure increases, the fluorescence signal increases, but the measured lifetimes experience no appreciable variation.

Conversely, when the electric power varies from 100 to 200 W, the measured lifetime decreases by about 30% while satellite lines due to excitation transfers increase correlatively. This effect is very likely due to the electrons of the discharge and may be controlled by making the lifetime measurements in a post-discharge. It is possible (Fig. 3) to turn the discharge off and to vary the delay t_L between the laser pulse and the discharge cutoff.

We have measured the variation of the $|\Delta J| = 1$ satellite lines intensities with t_L (Fig. 4). They decrease when t_L increases. They decrease more slowly when the pressure increases. They tend to a limit after a time which may be compared to the relaxation time of the electrons as calculated in such a plasma (Appendix). The limit

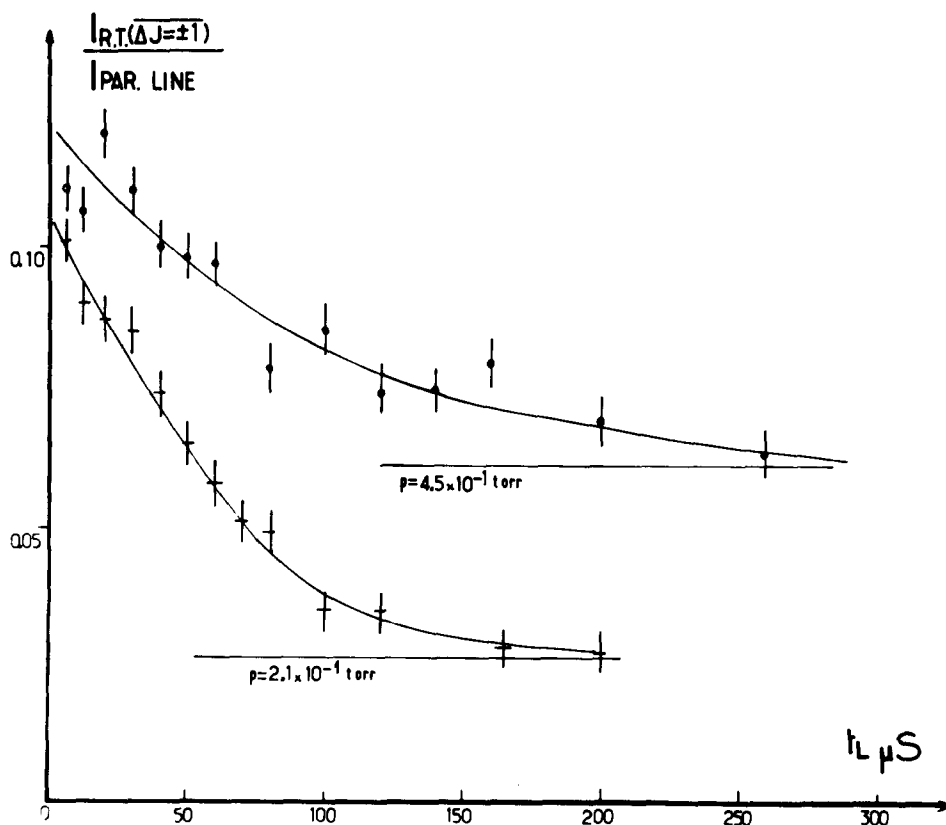


FIG. 4. The variation with t_L of the satellite lines intensities obtained by rotational transfer $\Delta J' = \pm 1$ from the corresponding parent line $J' = 8$, $v' = 10$.

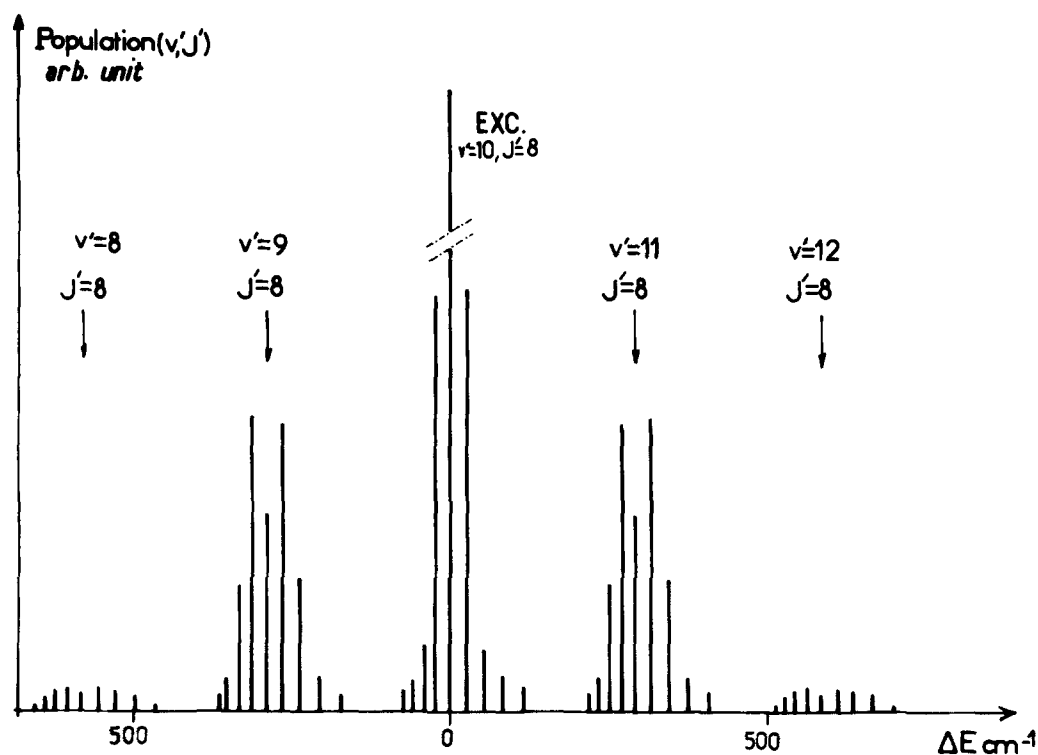


FIG. 5. The rotational and vibrational transfers attributed to the electrons in the discharge. The rotational transfers which remain in the post-discharge at $t_L = 120 \mu s$ have been subtracted. $v' = 10$, $J' = 8$, $P_{H_2} = 0.21$ Torr.

is due to the H_2 molecules and depends on the pressure.

A spectra obtained when the discharge is on (Fig. 5) shows the presence of vibrational transfer with $\Delta v' = \pm 1$ and $\Delta v' \pm 2$, which disappears in the post-discharge

when the electrons have disappeared. After the discharge is turned off the intensity of the fluorescence, with selective observation of one parent line, at first increases and then decreases (Fig. 6). It increases because the transfer due to the electrons decreases. It

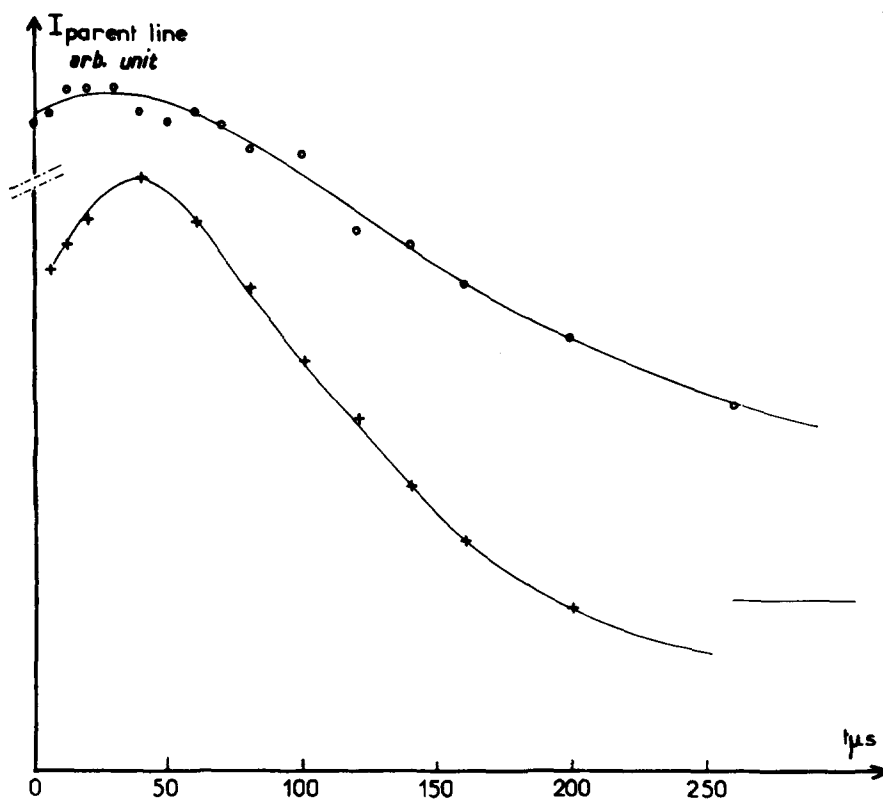


FIG. 6. The variation of a parent line intensity with t . $v' = 10$, $J' = 8$, $P_{H_2} = 0.21$ Torr \times , 0.45 Torr \circ .

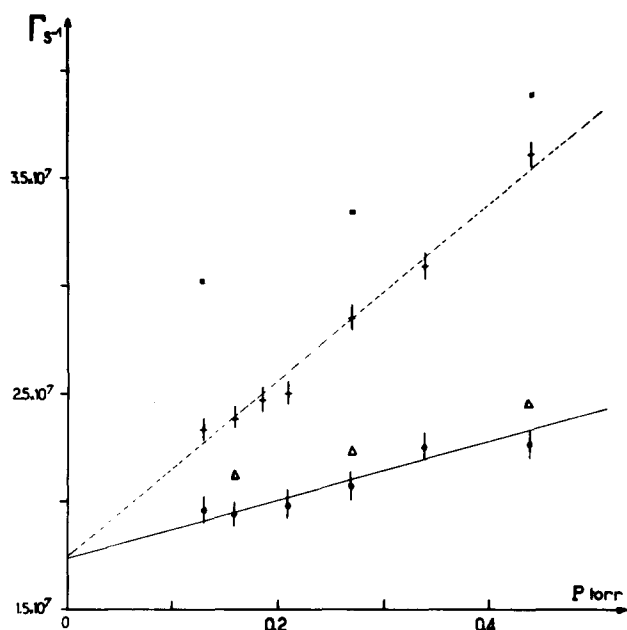


FIG. 7. Reciprocal lifetime values for $v'=10$, $J'=8$ at different H_2 pressures.

	Observation	Selective line	Broadband
Laser excitation			
In the post-discharge ($t_L = 120 \mu s$)	+	+	+
In the discharge		□	△

decreases because the hydride is no longer synthesized and diffuses through H_2 to the walls where it is destroyed. The relaxation times for this decrease are proportional to the H_2 pressure: 125 and 250 μs for 0.21 and 0.45 Torr, respectively.

In Fig. 7 we report reciprocal lifetime values obtained at various pressures in the post-discharge with $t_L = 120 \mu s$ or in the discharge. Observing selectively one parent line, the measured lifetimes are longer in the post-discharge than in the discharge, this difference decreasing when the pressure increases since the relaxation of the electrons at $t_L = 120 \mu s$ is not complete for the higher pressures used. If we observe a broadband (120 Å) including the parent lines and most of the satellite lines, the measured lifetimes at a given H_2 pressure are very similar in the discharge and in the post-discharge, and the extrapolated lifetime is the same as obtained by selective observation in the post-discharge. The variation of the lifetimes with the H_2 pressure is less important than it is with selective observation and the signal is much better. For these reasons, the systematic lifetime measurements have been made by broadband observation, obtained with a JOBIN-YVON H 20 monochromator. Its resolution is 40 Å/mm allowing for 120 Å observation with input and output slits of 1 and 3 mm, respectively. This broadband observation is sufficient to include all the satellite lines which appear in the post-discharge without any attenuation.

As the discharge fills the observation region, a spectrum observed with 0.2 Å resolution of the discharge light allows us to obtain the relative populations of the rotational levels in the KH ground state which provide the temperature of the molecule.⁸ The analyzed results (Fig. 8) show that the temperature is homogeneous, $T = 600 \pm 30$ K, i.e., the population follows a Boltzmann law over rotational energies greater than $2 \times kT$. This temperature may be considered as constant in the pressure range of the experiments. We suppose that the pressure is the same everywhere in the tube and that the local density of molecules is inversely proportional to the local temperature.

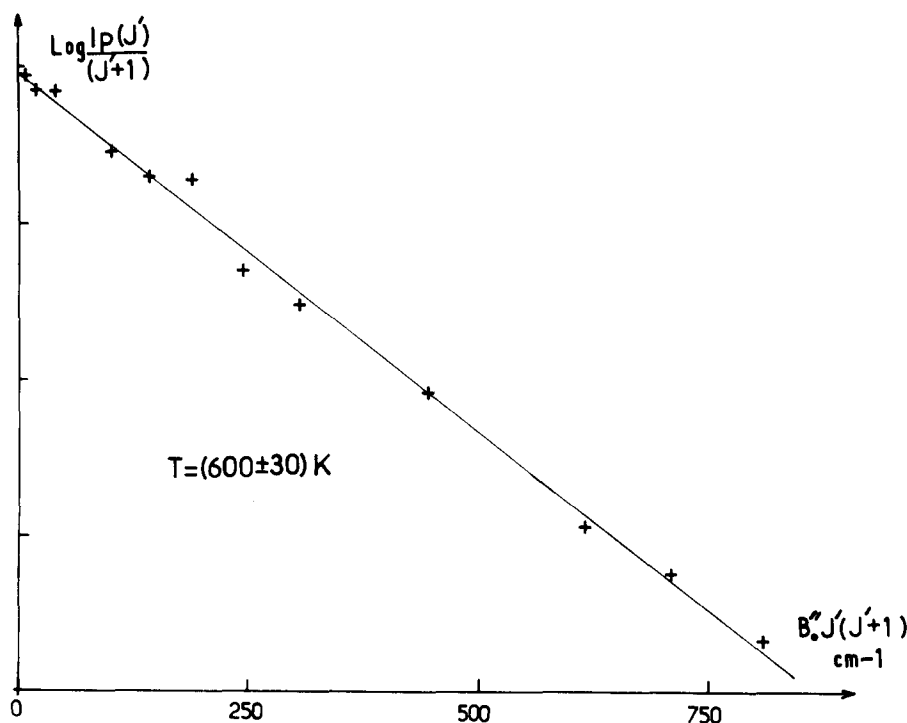


FIG. 8 Temperature measurement from P lines intensities in the discharge spectra KH, $A^1\Sigma^+ \rightarrow X^1\Sigma^+$, $P(11-0)$ transition.

TABLE I. Excitation and observation lines for lifetime measurements.

v' , (J')	Excitation $v'' \rightarrow v'$ $\lambda(\text{\AA})$ (R or P)	Observation $v' \rightarrow v''$ ($R+P$)	τ (ns)
5, (9)	$0 \rightarrow 5$ 5068,1 (P)	$5 \rightarrow 2$	64
7, (9)	$0 \rightarrow 7$ 4928,0 (P)	$7 \rightarrow 1$	60
10, (8)	$0 \rightarrow 10$ 4690,9 (R)	$10 \rightarrow 1$	58
13, (9)	$0 \rightarrow 13$ 4511,6 (R)	$13 \rightarrow 2$	56
17, (8)	$0 \rightarrow 17$ 4304,8 (P)	$17 \rightarrow 1$	54
19, (8)	$0 \rightarrow 19$ 4204,0 (P)	$19 \rightarrow 1$	53
22, (9)	$1 \rightarrow 22$ 4214,7 (R)	$22 \rightarrow 2$	34

In a similar experiment with BH in H_2 the rotational transfers and the lifetimes were the same in the discharge and in the post-discharge with t_L up to 200 μ s: the electrons had no effect on the excited state, and the thermal inertia was sufficient to keep the temperature constant up to this time t . With KH, as the rotational transfers remain constant after the relaxation time of the electrons, we shall suppose that the gas temperature does not vary.

At 600 K the vapor pressure of K is 0.6 Torr. In fact, the K pressure is much less as it is governed by the flow between the end of the cell heated by the magnetron power and the part of the glass tube at room temperature, towards the pump, where it deposits.

IV. RADIATIVE LIFETIMES

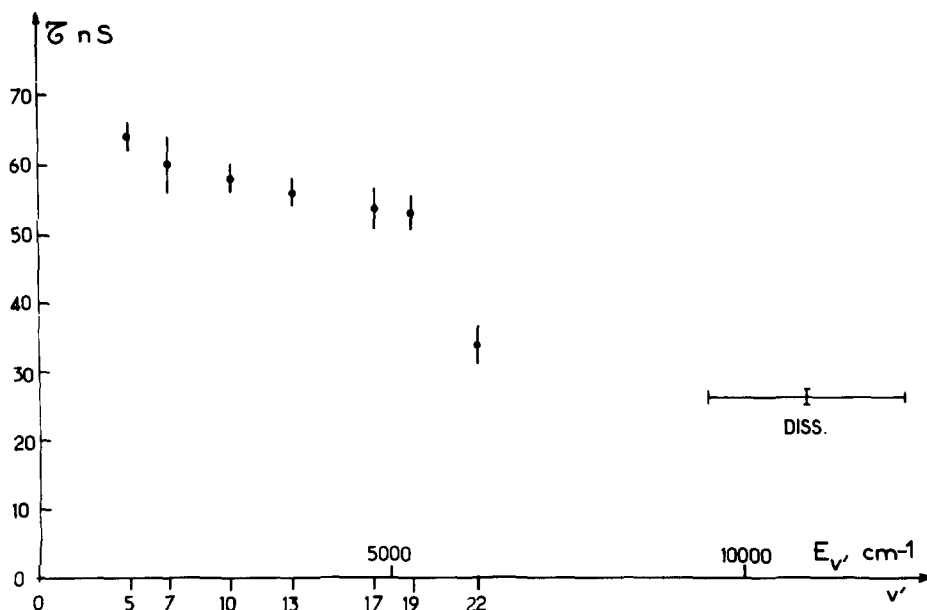
The studied levels and their radiative lifetimes τ are given in Table I with the corresponding excitation and observation lines. The variation of τ with the energy of v' is shown in Fig. 9. From $v'=5$ to $v'=19$, τ decreases slowly as $E(v')$ increases and tends to the lifetime⁹ of K 4^2P at the dissociation limit. The sudden decrease at $v'=22$ suggests the effect of a perturbation.

In LiH $A^1\Sigma^+$ the lifetimes have been calculated for all the v' , i.e., $\tau=29$, 36, and 27 ns for $v'=0$, 13, and 26, respectively.^{4,10} In KH $A^1\Sigma^+$ the variation of τ with v' is clearly different, and for low v' τ is two times greater than in LiH. The relative r location of the potential X and A energy curves are the same in the two molecules but their vertical energy separation ν from $A^1\Sigma^+ v'=0$ is two times smaller in KH than in LiH. As the transitions probabilities are proportional to $\nu^3 D^2$, the transition dipole moment D must be about 50% greater in KH than in LiH, as expected from the D values calculated in LiH,^{10,11} NaH,¹² and CsH.¹³ We are doing Franck-Condon and R-centroid calculations related to these results in KH and related also to new lifetime results in NaH. This work will be published in a following paper.

A perturbation of $A^1\Sigma^+$ at high v' by the dissociative $a^3\Sigma$ level is very likely to occur, as the corresponding potential energy curves calculated in NaH¹⁴ and in LiH¹⁵ are very close together in this region. Other lifetime measurements would have confirmed this hypothesis to justify the decrease of the lifetime at $v'=22$. They have not been possible with the present experiment.

V. QUENCHING

The lifetimes obtained by broadband observation in the post-discharge show a reduction with the H_2 pressure which may be attributed to the quenching of the KH excited state by transfer to the H_2 vibrational states. In the discharge these lifetimes are slightly smaller than

FIG. 9. The variation of the KH $A^1\Sigma^+$ radiative lifetimes $\tau_{v'}$ with v' .

in the post-discharge. The difference may be justified by the few satellite lines $\Delta v' \neq 0$ which in this case are out of the monochromator bandwidth showing that the electrons provide no appreciable quenching.

VI. ROTATIONAL TRANSFERS

The rotational transfers obtained in the post-discharge are due to H_2 . In the discharge they are due both to H_2 and to the electrons. We shall do a few comments about the relative populations of the levels excited by these transfers.

For collisions with electrons in the "time independent diffusion theory"¹⁶ and for collisions with neutral particles in the "time dependent first order perturbation theory"¹⁷, the cross-sections $\sigma_{i \rightarrow f}$ depend on the interaction matrix element square $|\langle i | V | f \rangle|^2$ between the initial and the final states. The V may be expanded over spherical harmonics

$$V_{(R, \theta)} = \sum_{LM} V_M^L(R) Y_M^L(\theta) \quad (1)$$

As $\Lambda = 0$ for a Σ state, the collision cross section is

$$\sigma_{J_i \rightarrow J_f} = \sum_L A^L A^{L*} \begin{pmatrix} J_i & L & J_f \\ 0 & 0 & 0 \end{pmatrix}^2 (2J_f + 1) \quad (2)$$

The $3J$ symbol describes the addition of the angular momentum L in the reference frame of the molecule. $J_i + L + J_f$ must be even. The even (odd) L provide rotational transfers with no change (change) of parity. The A^L are the scattering parameters which depend on the symmetry of the interaction. The $L = 1$ and $L = 2$ terms have the symmetry of a dipole and of a quadrupole, respectively. Odd values of L may occur in polar molecules only.

The value of the electric dipole moment μ of KH $A^1\Sigma^+$ is not known but may be approximated from experimental and theoretical results in other alkaline hydrides, NaH^{19} and $LiH^{10,11,20}$: $\mu \approx 0$ for $E_v \approx 0$, and $\mu \approx 2$ a.u. for $E_v \approx 5.500 \text{ cm}^{-1}$. These E_v are the limit values for KH, $A^1\Sigma^+$, $v' \leq 19$.

A. By hydrogen molecules

In the post-discharge, by selective line observation, the reduction of the lifetime with the H_2 pressure is due both to the quenching and to the rotational transfers. No vibrational transfers are observed. The collision cross sections may be found as we measure the reduction of the lifetime at a known pressure and temperature, with no electrons present, providing the collision probabilities $\Gamma_{\text{quenching}}$ by broad band observation, or $\Gamma_{\text{rotational}}$

TABLE II. Quenching (σ_Q) and rotational (σ_{rot}) cross sections for KH $A^1\Sigma^+$ with H_2 at (600 ± 30) K.

v'	J'	$\sigma_Q (\text{\AA}^2)$	$\sigma_{\text{rot}} (\text{\AA}^2)$
5	9	57 ± 6	41 ± 10
10	8	34 ± 4	68 ± 12
19	8	45 ± 5	92 ± 15

TABLE III. Partial rotational cross sections for KH $A^1\Sigma^+$, $v' = 10$, $J' = 8$ with H_2 at (600 ± 30) K.

J'	4	5	6	7	9	10	11	12
$\sigma_{8 \rightarrow J'} (\text{\AA}^2)$	2.5	5.5	8.0	17.5	17.9	8.1	5.4	2.6

+ $\Gamma_{\text{quenching}}$ by narrow line observation. The rotational σ_{rot} and quenching σ_q are given in Table II. The definition of the cross section is given by the formulas

$$\Gamma_{\text{coll}} = \sigma \cdot N \cdot \langle v \rangle, \quad \langle v \rangle = \left[\frac{8}{\pi} RT \left(\frac{1}{M_{\text{KH}}} + \frac{1}{M_{H_2}} \right) \right]^{1/2} \quad (3)$$

The total rotational transfer cross-sections σ_{rot} increase from $v' = 5$ to $v' = 19$ as very likely do the permanent electric dipole moments of these vibrational levels.

The partial cross sections for the rotational transfers to the various J' levels are given in Table III. Their relative values are obtained from a spectra in the post-discharge. Their absolute values are calibrated from σ_{rot} . A verification of these results may be obtained by comparison of the parent and satellite lines as the radiative lifetime is known. The signal obtained by time integration of the fluorescent light is proportional to (N_0/Γ) the mean number of excited molecules (N_0 total number of molecules excited by a laser pulse). Then

$$\frac{I_{\text{parent}}}{I_{\text{total}}} = \frac{\Gamma_{\text{rad}} + \Gamma_{\text{quench}}}{\Gamma_{\text{rad}} + \Gamma_{\text{rot}} + \Gamma_{\text{quench}}} \quad (4)$$

The partial cross sections are symmetric in $\Delta J'$. For the observed rotational transfers limited to $|\Delta J| = 4$, the energy difference $|E_f - E_i| < 115 \text{ cm}^{-1}$ is smaller than the kinetic energy which is in this case of the order of $kT \approx 400 \text{ cm}^{-1}$ at 600 K. The endothermicity for $J_f \geq J_i$, or the attenuation of the transition probability due to the duration of the collision have a negligible effect in this case.^{17,21}

The partial cross sections decrease monotonically when $|\Delta J'|$ increases as in alkaline dimers.^{21,22} This was not the case in BH^{23} where the transfers to levels of the same parity as the initial level were privileged. Two obvious reasons may justify this difference. The alkaline hydrides, due to the contribution of a ionic bond, may have a polar character more important than $BH^1\Pi$ $v' = 0$ ($\mu = 0.22$ a.u.) which has a covalent bond.²³ On the other hand, the cross section is more than two times greater for KH than for BH. Successive transfers at each collision are more likely to occur. In this case, the perturbation theory has to be used in higher order than first order and the propensities are attenuated.

B. By electrons

It is not possible to obtain the cross sections for the transfers due to the electrons as we do not know their density and their speed. We can only compare the populations of the v' and J' levels excited by the transfers due to the electrons in the experimental conditions of our discharge.

To obtain the rotational transfer populations due to

the electrons from the line intensities in the discharge we have to subtract the satellite line intensities due to transfers with H_2 in the post-discharge at the same pressure with a recalibration so that the sum of all the lines are fitted to be the same in the two cases. Figure 5 shows the rotational and the vibrational transfers due to the electrons.

The interaction potential is simply due to the interaction of the electron charge with the molecular electric parameters: the permanent electric dipole moment providing the $V^{L=1}$ term in Eq. (1), the electric quadrupole moment and the polarizability anisotropy providing the $V^{L=2}$ term.

The rotational $\Delta J = \pm 1$ transfers are much more probable than the other ΔJ transfers (Fig. 5). This result is to be expected in polar molecules¹⁶ with $V^{L=1}$ as pre-dominant interaction term.

VII. VIBRATIONAL TRANSFERS

They are due to the electrons only. In Fig. 5 the symmetric decrease as $|\Delta v'|$ increase suggests that this variation is not due to the $|\Delta E|$ variation but to the Franck-Condon factors variation. In fact, the energy of the electrons is much greater than ΔE .

In the $|\Delta v| = 1$ transfers, the $|\Delta J'| = 1$ is the most important due to the charge-dipole interaction, whereas the $|\Delta J'| = 0$ is less important than its neighbors. From the $|\Delta J'| = 2$ and $|\Delta J'| = 4$ levels populations it is possible to fit the A^L parameters for $L=2$ and $L=4$ and to calculate their contribution to the $\Delta J' = 0$ transition, from the relative values of the $3J$ symbols.¹⁷ They are found to be about the half of the experimental $\Delta J' = 0$ transfer. The other half may be due to the contribution of vibrational excitation transfers by dissociative attachment of slow electrons.¹⁸ This experiment provides the contribution of vibrational transfers without addition of angular momentum compared to the vibrational transfers with addition of angular momentum, i.e., about 10%.

The $\Delta v' \neq 0$ bands are broader than the $\Delta v' = 0$ band. The explanation is very likely to be the same as for transfers in Li_2 with rare gases²²: the more violent collisions transfer more angular momentum both into and out of the molecules.

ACKNOWLEDGMENT

We acknowledge N. Sadeghi-Kharrazi for discussion about plasma problems.

APPENDIX

The relaxation of the charged species in high frequency discharges in rare gases has already been studied in our laboratory.²⁴ In the present case, the discharge takes place in a mixture of K and H_2 . The energies of the electrons are inhomogeneous but they are limited by the ionization energy of K, 4.34 eV. We suppose^{24,25} that the electron-ion recombination occurs on the walls and, when the electric power is turned off, that the electrons

and the ions diffuse together (ambipolar diffusion) through H_2 in a quasineutral plasma. We suppose that the density of the charges decreases exponentially with the same relaxation time τ everywhere in the cell,

$$N = N_0(x, y, z) e^{-t/\tau}.$$

The formulas used to calculate τ are found in Ref. 24.

The time dependent equation in the ambipolar case

$$\delta N / \delta t = \nabla \cdot (\mathcal{D}_a \nabla N)$$

gives

$$\nabla \cdot (\mathcal{D}_a \nabla N_0) = N_0 / \tau.$$

If \mathcal{D}_a does not depend on the localization in the discharge, the time independent diffusion equation is

$$\nabla^2 N_0 + (N_0 / \mathcal{D}_a \tau) = 0.$$

The solution depends on the geometry of the cell. τ depends on \mathcal{D}_a and on a diffusion length Λ :

$$\mathcal{D}_a = \Lambda^2 / \tau.$$

The ambipolar diffusion coefficient \mathcal{D}_a is proportional to $\sqrt{T_e}$ and in inverse ratio to the neutral gas density.

For a cylinder of infinite length and radius R ,²⁴ $\Lambda = R/2.4$. As the mobility μ_e of the electrons is much greater than the mobility of the ions μ_+ ,

$$\mathcal{D}_a \approx \mathcal{D}_+ \left(1 + \frac{T_e}{T_+} \right).$$

For the ambipolar diffusion of K^+ in H_2 the experiment²⁶ gives $\mu_+ = 17.5 \times (M_r)^{-1/2}$, where M_r is the reduced mass of K and H_2 , at $T = 290$ K, for a H_2 density $N_{H_2} = 2.69 \times 10^{19} \text{ cm}^{-3}$. The diffusion coefficient is related to the mobility by the general Einstein equation $\mathcal{D} = \mu kT/e$, where k is the Boltzmann constant and e the electron charge.

In the case where the electrons are in thermal equilibrium with the gas $T_e = T_{\text{gas}}$, i.e., $\mathcal{D}_a = 2\mathcal{D}_+$, if $T = 600$ K, $R = 1.75$ cm, we obtain for $P = 0.2$ and 0.45 Torr, $\tau = 84$ and 180 μs , respectively, which is an upper limit as $T_e \geq T_g$. The thermalization of the electrons by collision with the gas is given by²⁴

$$\frac{T_e}{T_g} \approx \sqrt{\frac{1 + e^{-2at}}{1 - e^{-2at}}},$$

with

$$a = \frac{m_e v_e \sigma N_{H_2}}{M_{H_2}},$$

v_e is the mean speed of the electrons at $T = 600$ K, σ is the elastic cross section¹⁸ of e with H_2 , $\sigma \approx 10 \text{ \AA}^2$. The vibrational and rotational transfer cross sections are negligible. At $P = 0.2$ Torr, to obtain $T_e/T_g = 1.1$ the time t is 25 μs which is shorter than the laser delay t_L . Effectively, the relaxation times in the experiment (Fig. 6) are close to those calculated above for thermal electrons.

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