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The infrared spectrum of KH^{a)}

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Reported here is the first observation of the infrared spectrum of KH. Fundamental bands and first hotbands of the ³⁹KH and ⁴¹KH isotopic forms were measured at high resolution using a diode laser based spectrometer. An ac glow discharge through potassium vapor and hydrogen gas was used to produce KH. A combined isotopic Dunham coefficient analysis was used to fit all the spectra, with the Dunham coefficients for ³⁹KH coming out as $Y_{10} = 985.6714(30) \text{ cm}^{-1}$, $Y_{20} = -14.9013(10) \text{ cm}^{-1}$, $Y_{01} = 3.41640(10) \text{ cm}^{-1}$, $Y_{11} = -0.085313(26) \text{ cm}^{-1}$, $Y_{21} = 5.41(60) \times 10^{-4} \text{ cm}^{-1}$, $Y_{02} = -1.6354(36) \times 10^{-4} \text{ cm}^{-1}$, $Y_{12} = 1.13(10) \times 10^{-6} \text{ cm}^{-1}$, $Y_{03} = 7.6(8) \times 10^{-9} \text{ cm}^{-1}$, (quoted at 2σ error limits). A bond length of $2.241152(16) \text{ \AA}$ and a Dunham corrected value for ω_e of $986.0505(30) \text{ cm}^{-1}$ are obtained. The pressure broadening of KH by H₂ and the chemistry of KH formation in the glow discharge plasma are also discussed.

INTRODUCTION

Only for LiH has the infrared spectrum of an alkali metal hydride been previously reported.¹ For elemental diatomic hydrides in general, only ten have directly observed infrared spectra out of the over 100 possible, which is quite surprising in view of the fundamental role that hydrides have played in understanding molecular structure and in view of their continued importance in theoretical investigations of heavy element chemical bonding and in computational development of pseudopotential methods.²⁻⁷ There are, of course, numerous optical studies of hydride electronic spectra,⁸ yet their infrared absorption spectra would be most welcome not only for the high precision molecular constants and structural features obtained, but also for identification of the ground state electron spin and orbital symmetries which are of central interest in the transition metal hydrides to the right of potassium in the Periodic Table.⁷

The KH $A \Sigma^+ - X \Sigma^+$ electronic spectrum has been the subject of a number of studies, starting with the arc discharge emission work of Almy and Hause.⁹⁻¹⁸ Recently, Giroud and Nedelec¹⁷ have carried out time resolved fluorescence studies of KH in a microwave discharge and in this way measured the A state vibronic lifetimes as well as vibrational and rotational energy transfer with H₂ and plasma electron. Regarding theoretical structure calculations, there have been several pseudopotential studies,^{3,4,19,20} a reported valence bond calculation,²¹ and an FSGO SCF study.²² There is, however, no currently available high quality all electron calculation on KH that is comparable to those for LiH and NaH.²³⁻²⁵ Stwalley and co-workers have generated RKR potential energy curves for KH and the other alkali hydrides,²⁴⁻²⁹ with their analysis for KH²⁶ being particularly helpful to us. Of other high resolution work on alkali hydrides, which includes electric resonance for LiH³⁰⁻³² and pure rotation for LiH and NaH,^{33,34} the submillimeter investigation by Sastry, Herbst, and DeLucia³⁴ is especially

noteworthy here, as their success in producing NaH in a dc glow discharge encouraged our efforts.

The gas phase formation of alkali metal hydrides from metal atoms and H₂ is, at present, poorly understood. The three methods used so far to generate the hydrides, namely, with ovens,^{1,15} in discharges,^{9,16,34} and, recently, by laser induction,³⁵⁻³⁷ are surely related. So in addition to our reports on the observed spectrum, the derived molecular constants and the pressure broadening of KH by H₂, we will also discuss the formation and loss mechanisms for KH and model these by a simple steady state analysis.

DISCHARGE CELL AND SPECTROMETER

The ac power circuit, glow discharge cell, and infrared spectrometer are shown in Fig. 1. Basically, a discharge through ~ 4 Torr of H₂ heats potassium metal chips dispersed along the cell, as in Ref. 34. After about 30 s the potassium apparently vaporizes turning the cell a distinct blue-green color, presumably the $A-X$ emission of KH. (The strength of the infrared absorption signals was always correlated with this color.) The infrared spectrum is observed with Doppler (and laser linewidth) limited resolution from 9.5 to 12 μ wavelengths by a Laser Analytics LS-3 based diode laser spectrometer.

In more detail, the sine wave output of a function generator is amplified by a Tecron 7610 PA amplifier (power of 1 kW). The purpose of the transformer circuit is to simultaneously match the glow discharge impedance (10–20 k Ω) to the output of the amplifier (2–8 Ω), while boosting the ac voltage for discharge ignition and sustained operation. The watercooled, wirewound resistors R_1 and R_2 provide the necessary impedance matching and power transfer control, and the ac capacitor C_1 is a safety measure to protect the amplifier. Counterwiring the resistors, as indicated, avoids radiative broadcast by the coils which can be picked up by the diode laser circuitry and lead to an unwanted frequency modulation. The discharge voltage (measured by the divider R_4 and R_5) and the discharge current (the drop over R_3) are shown in Fig. 2, with a plateau to plateau voltage of 5 kV and a peak to peak current of 0.52 A for a frequency of 1.1 kHz.

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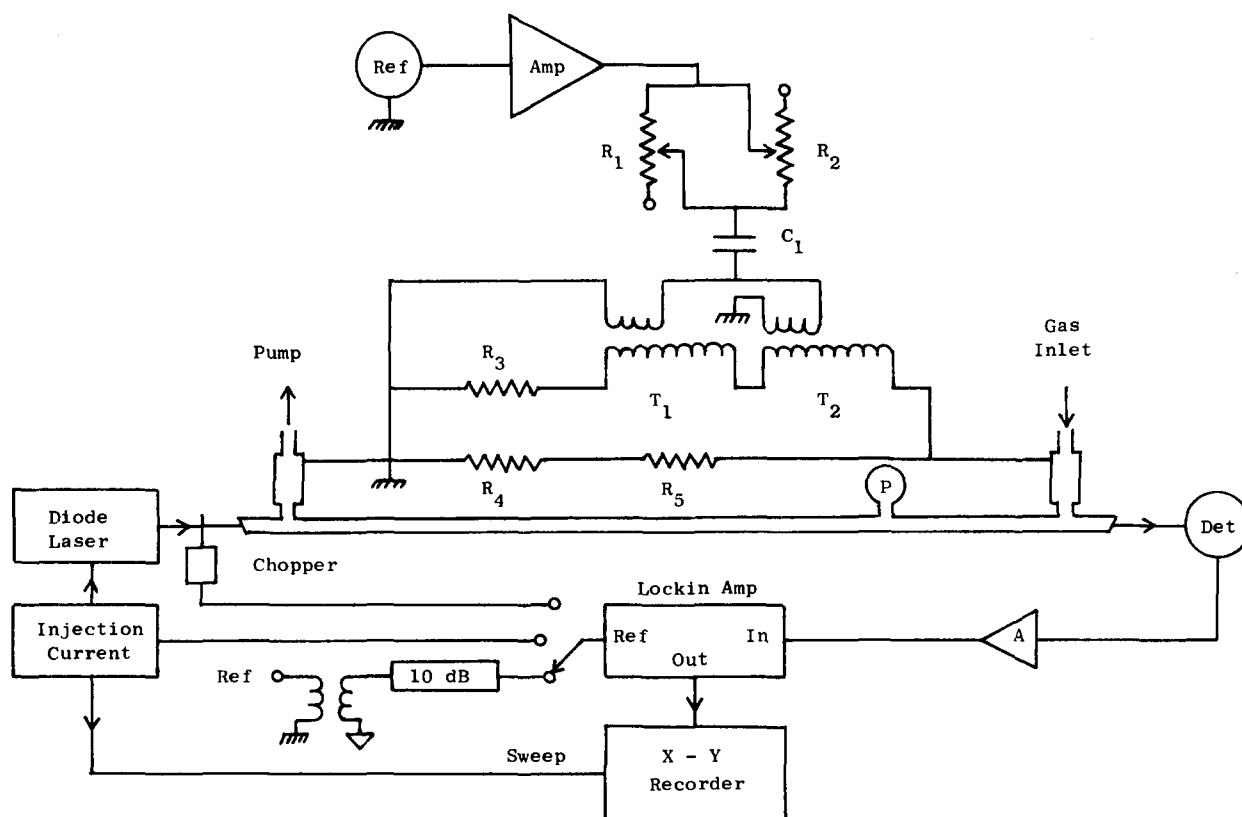


FIG. 1. Discharge cell and spectrometer. R_1 and $R_2 = 18 \Omega$; $R_3 = 10 \Omega$; $R_4 = 100 \text{ k}\Omega$; $R_5 = \text{M}\Omega$; $C_1 = 38 \mu\text{F}$. T_1 and T_2 are UTC type S-60 transformers (1:22).

Note that the discharge is on twice each cycle and that it completely extinguishes once the applied voltage drops below threshold. Apart from the ignition transients, the discharge voltage waveform of a clipped sine wave is expected because the discharge acts as a constant voltage circuit element.³⁸ As a consequence, the current waveform closely follows the further sinusoidal application of power. We have found that glow discharges with this experimental arrangement run from 10 Hz to 40 KHz, the limitation being largely due to the matching network employed. We also found that waveform quality is highly dependent upon the suitability of transformer circuit elements for high voltage, high audio power operation.

A Pyrex glass tube (12 mm o.d., 1.5 mm wall, 70 cm from T to T) forms the cell. It is not cooled and is evacuated

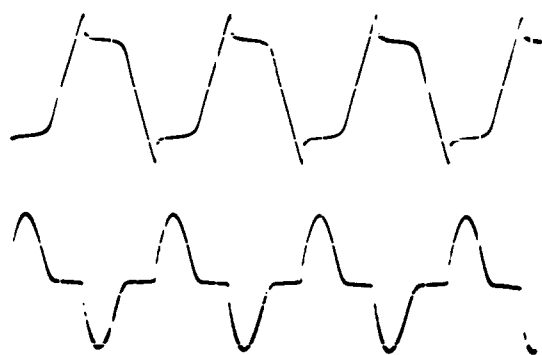


FIG. 2. Oscilloscope trace of discharge voltage (top) at 5 KV pp and the discharge current (bottom) at 0.52 A pp. The discharge frequency is 1.1 KHz with $P = 4$ Torr.

by a throttled mechanical pump ($70 \text{ cm}^3/\text{s}$) to conserve the potassium load against entrainment in the gas flow and exhaustion to cooler regions. Symmetric brass electrodes (7/8 in. o.d., 1/8 in. wall, 6 in. long) are water cooled for their cathode cycle heating and are placed off axis for sighting and cleaning advantages. In operation, the initial peak to peak voltage of 7.5 kV reduces to 5 kV as the blue-green color begins. Using a glass enshrouded thermocouple submerged in the plasma from one end, the gas temperature was measured to be $\sim 630 \text{ K}$ in a pure H_2 discharge and $\sim 510 \text{ K}$ in the $\text{K} + \text{H}_2$ glow. These values are in reasonable agreement with earlier probe measurements³⁹ and with recent linewidth measurements on a variety of ions using a higher spectral purity laser source.⁴⁰

Radiation was provided by two Laser Analytics mesa stripe geometry lead salt diodes and was detected by a HgCdTe photoconductive detector ($\lambda_{\text{max}} = 11.5 \mu$). Once optimum conditions for producing KH were established ($P = 4$ Torr and 200–250 W of discharge power at 1 kHz), the fundamental vibration-rotation transitions were easily observed on an oscilloscope sweep. A chopper modulated video recording of this is given at the top of Fig. 3. The spectrum just below is the usual (source) frequency modulated spectrum detected at $2f$. The bottommost trace is a KH density modulated spectrum, obtained by simply sweeping the laser frequency and detecting synchronously for infrared power absorption at twice the discharge frequency. The signal magnitude is the same as the fully modulated source spectrum above.

The fully developed density modulated spectrum is due

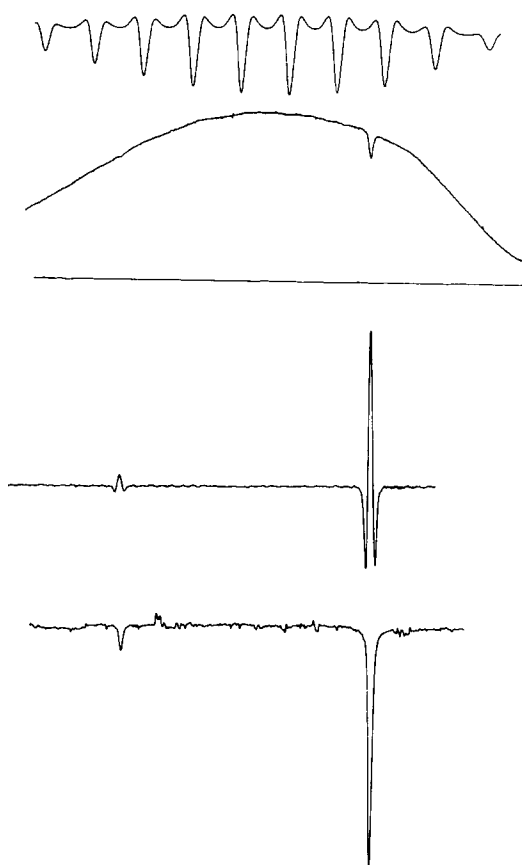


FIG. 3. Infrared spectra of the P(6) K-39 fundamental at 912.994 cm^{-1} (strong line to right) and the P(2) K-39 hotband line at 912.749 cm^{-1} (feature at left). Top—Chopper modulated spectrum with the flat baseline at the zero of power and with the 1 in. germanium etalon transmission at the very top ($\text{FSR} = 0.048\text{ 18 cm}^{-1}$). Middle—Laser frequency modulated spectrum detected at $2f$. Bottom—Density modulated spectrum with detection at $2f$. A time constant of 0.1 s and a scan rate of 5 s per full linewidth was employed in all the scans.

to the generation and loss of KH at twice the discharge frequency. This is consistent with a gas phase chemical synthesis and with the discharge current waveform in Fig. 2. We expect the major loss of KH to be by diffusion to the tube wall with irreversible precipitation or further reaction. An estimate of the time associated with this wall loss comes from

$$\tau_w = \frac{(r/2.405)^2}{D},$$

where r is the tube radius and D is the diffusion coefficient. We estimate D for KH in H_2 by using a method that accounts for the long range intermolecular forces between the two.⁴¹ We obtain $200\text{ cm}^2\text{ s}^{-1}$ for the experimental conditions here and $0.34\text{ cm}^2\text{ s}^{-1}$ at STP, which is in the range of $0.3\text{--}0.5\text{ cm}^2\text{ s}^{-1}$ known for most molecules in H_2 .⁴² The resulting τ_w of 0.17 ms is comparable to the dead time between current fall and current rise pulses in Fig. 2, $\sim 0.19\text{ ms}$. Our observation that discharge frequencies of 1 to 2 KHz gave the best density modulated spectra is consistent with this loss of KH. Loss of plasma electrons and ions due to ambipolar diffusion is much faster, $5\text{--}10\text{ }\mu\text{s}$, and is consistent with the ever-slight distortion of the current peaks in Fig. 2. At the discharge frequency, there is a $1f$ component in the KH infrared absorption lines, and it has the same line shape as the $2f$ signal, but attenuated by about a factor of 100. This $1f$ re-

sponse is quite likely due to remaining asymmetries in the discharge conditions between the two half cycles, and the resulting difference in KH produced giving the $1f$ response. Related uses of density, or molecular, modulation employed for infrared detection have been reported by Podolske and Johnston⁴³ and by Hirota and co-workers.⁴⁴

SPECTRA AND ANALYSIS

Listed in Table I are the measured infrared frequencies of the K-39 and K-41 isotopes of KH, both for their fundamental bands and their first hot bands. The missing transitions in the usual P and R branch sequences are due to gaps in the diode laser performance. Unfortunately, the diode coverage was more favorable in the R branches of these bands, leading to the imbalance in line coverage. The transition frequencies were established by comparing frequency

TABLE I. Infrared transition frequencies (cm^{-1}).

³⁹ KH $v = 1 \leftarrow 0$		⁴¹ KH $v = 1 \leftarrow 0$	
R (18)	1047.875	R (18)	1047.213
R (17)	1044.938	R (17)	1044.280
R (16)	1041.772	R (16)	1041.119
R (15)	1038.385	R (15)	1037.731
R (14)	1034.770	R (14)	1034.120
R (13)	1030.937	R (13)	1030.286
R (12)	1026.882	R (12)	1026.237
R (11)	1022.614	R (11)	1021.972
R (10)	1018.135	R (10)	1017.500
R (9)	1013.446	R (9)	1012.814
R (8)	1008.559	R (8)	1007.927
R (7)	1003.461	R (7)	1002.838
R (6)	998.165	R (6)	997.549
R (5)	992.680	R (5)	992.071
R (4)	987.002	R (4)	986.394
R (3)	981.127	R (3)	980.528
R (2)	975.084	R (2)	974.491
P (1)	949.120	R (1)	968.271
P (6)	912.994	P (6)	912.389
P (8)	897.504		
P (9)	889.552		
P (10)	881.466		
P (11)	873.251		
P (13)	856.455		
P (16)	830.374		
³⁹ KH $v = 2 \leftarrow 1$		⁴¹ KH $v = 2 \leftarrow 1$	
R (24)	1027.310	R (17)	1011.880
R (22)	1024.257	R (14)	1002.103
R (20)	1020.254	R (12)	994.492
R (19)	1017.898	R (11)	990.365
R (17)	1012.501	R (10)	986.030
R (15)	1006.198	R (7)	971.802
R (14)	1002.714	R (6)	966.665
R (13)	999.012	P (2)	912.230
R (12)	995.094		
R (11)	990.965		
R (10)	986.628		
R (9)	982.082		
R (8)	977.336		
R (7)	972.388		
R (6)	967.248		
R (3)	950.681		
R (2)	944.789		
R (0)	932.481		
P (2)	912.749		
P (10)	853.438		
P (11)	845.422		

TABLE II. Dunham coefficients for ^{39}KH (in cm^{-1}).^a

$Y_{10} = 985.671\ 4(30)$
$Y_{20} = -14.901\ 3(10)$
$Y_{01} = 3.416\ 40(10)$
$Y_{11} = -0.085\ 313(26)$
$Y_{21} = 5.41(60) \times 10^{-4}$
$Y_{02} = -1.635\ 4(36) \times 10^{-4}$
$Y_{12} = 1.13(10) \times 10^{-6}$
$Y_{03} = 7.6(8) \times 10^{-9}$

^a Statistical error estimates at 2σ are right justified.

offset from known D_2CO and OCS lines,^{45,46} using a germanium etalon. Individual line position accuracy is expected to be $\pm 0.005\ \text{cm}^{-1}$ in this initial spectrum discovery work, an error that can be reduced by at least a factor of 10.

To within the present line position accuracy and distribution, all 72 lines in Table I can be simultaneously fit with eight independent, mass reduced Dunham coefficients in the molecular vibration-rotation energy formula

$$E(v, J) = \sum_{kl} \left[Y_{kl} \mu^{\frac{k}{2} + l} \right] \times \left[\mu^{-\left(\frac{k}{2} + l\right)} (v + 1/2)^k (J(J+1))^l \right],$$

where μ , v , and J have their usual significance. The first factor in each term is the mass reduced Dunham coefficient (the same as Stwalley's Z_{klo} ⁴⁷), and the second factor corresponds to the mass reduced quantum numbers (Stwalley's η and ξ) ($\mu^{39} = 0.982\ 414\ 316\ \text{amu}$ and $\mu^{41} = 0.983\ 624\ 096\ \text{amu}$). The resulting Dunham coefficients for ^{39}KH are given in Table II, with the errors quoted at 2σ , or at the 95% confidence limit. Note that twice the standard deviation ($2(0.002\ 47\ \text{cm}^{-1})$) corresponds well to our anticipated line position accuracy. (Only three of the 72 lines, or 4%, were outside the 2σ confidence limit.) All of the higher order coefficients are of the order of magnitude expected from approximate relations involving the lower order terms.⁴⁸ (The same coefficients for ^{41}KH can be obtained by reduced mass scaling.) The differences between the results in Table II from those that would be obtained from a comparable fit of purely ^{39}KH data are less than the quoted errors (as can be anticipated from isotope scaling known results for the related $\text{H}^{35}\text{Cl} - \text{H}^{37}\text{Cl}$ case: $Y_{10}^{35}/Y_{10}^{37} = (\mu^{37}/\mu^{35})^{1/2}$ to within three parts per million,⁴⁹ $Y_{01}^{35}/Y_{01}^{37} = (\mu^{37}/\mu^{35})$ to within ten parts per billion,⁵⁰ ..., all within the errors given in Table II.)

LINE INTENSITY AND KH DENSITY

The density of KH, n_{KH} , can be estimated from the fractional infrared absorption $\Delta I/I$ and the infrared absorption cross section σ_{IR} by

$$\Delta I/I = \sigma_{\text{IR}} n_{\text{KH}} L$$

and

$$\sigma_{\text{IR}} = 5.46 \times 10^{-13} \mu^2 \sqrt{\frac{M}{T}} \left(f_l - \frac{g_l}{g_u} f_u \right) \text{cm}^2,$$

where L is the path length (cm), μ is the transition dipole moment (D), M is the mass (amu), T is the temperature (K), and f and g are the fractional populations and degeneracies

of the upper and lower states. The fundamental band transition moments for LiH and NaH have been theoretically evaluated using very accurate methods.²³⁻²⁵ Since no such calculation is available for KH, we estimate the rotationless value for KH to be 0.35 D, based upon the LiH and NaH work. When squared and reduced by the appropriate rotational factor of 6/13 for the $P(6)$ transition in Fig. 3, we have $\mu^2 = 0.057\ \text{D}^2$. With a temperature of 510 K, the $P(6)$ absorption cross section computes to be $6.8 \times 10^{-16}\ \text{cm}^2$. For the 18% absorption shown at the top of Fig. 3, a column density ($n_{\text{KH}} L$) of $2.6 \times 10^{14}\ \text{cm}^{-2}$ results. Assuming uniform density along the 70 cm path, we have $n_{\text{KH}} = 4 \times 10^{12}\ \text{cm}^{-3}$, or a 0.2 mTorr partial pressure. The relative intensities of the hotband and fundamental lines in Fig. 3 give a vibrational temperature of 550–650 K, quite near the probe measurement and translational equilibrium.

LINEWIDTH AND PRESSURE BROADENING

In Fig. 4 the half-width at half-maximum $\Delta\nu$ for the density modulated spectrum of the $P(6)$ fundamental is plotted up to 10 Torr, our capacitance manometer limit. As the pressure increases, there is quite likely a slight rise in discharge temperature of as much as $\sim 10\%$ from 2 to 10 Torr, based upon earlier studies.³⁹ There are three contributions to the linewidth. First, the half-width has a Doppler broadening contribution $\Delta\nu_d$ of 35 MHz at 510 K. Second, the finite emission linewidth of the laser $\Delta\nu_l$ can add 10–50 MHz.⁵¹ Third, there is the pressure broadening contribution $\Delta\nu_p$, which is largely due to collisions of KH with H_2 . Through the uncertainty relation and the collision frequency, we have

$$\frac{\Delta\nu_p}{P} = \frac{1}{RT} \frac{\sigma_c v}{2\pi},$$

where R is the gas constant ($1/R = 9.648 \times 10^{18}\ \text{cm}^{-3}\ \text{Torr}^{-1}\ \text{K}$), σ_c the pressure broadening cross section, and v the relative velocity. By using Kieffer and Bushkovitch's⁵² quasiresonant σ_c due to the dipole-quadrupole intermolecular force and then integrating $\sigma_c v$ over a Boltzmann distribution of velocities, we have

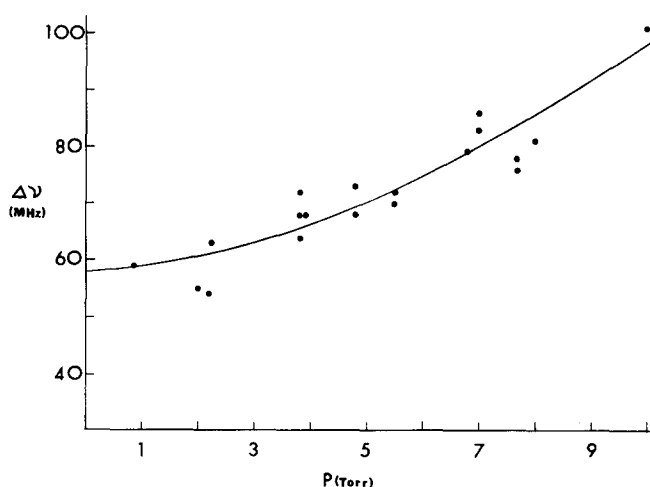


FIG. 4. The half-width at half-maximum of the $P(6)$ K-39 (in MHz) is plotted vs the discharge pressure (in Torr). The standard deviation of the fitted line is 4.4 MHz.

$$\frac{\Delta\nu_p}{P} = \frac{(3/5)^{1/3} \Gamma(3/5)}{\sqrt{\pi} RT} \left(\frac{\mu_1 Q_2}{\hbar} \right)^{2/3} \left(\frac{2k_B T}{m} \right)^{1/6},$$

where $\Gamma(3/5)$ is the gamma function at $3/5$, 0.9033 , μ_1 is the electric dipole moment of KH, Q_2 is the electric quadrupole moment of H_2 , \hbar is Planck's constant over 2π , k_B is Boltzmann's constant, and m is the reduced mass. We estimate the dipole moment of KH to be 7 to 8 D, based upon previous work for LiH and NaH,^{23–25,30} but it could be as much as 10 D.²² Kieffer and Bushkovitch point out in their paper⁵² that their cross section could be high by as much as 30%. With these considerations in mind and with a quadrupole moment for H_2 of 0.80×10^{-26} esu cm²,⁵³ we expect $\Delta\nu_p/P$ to be 5 to 9 MHz/Torr. Employing the approximate combining relation $\Delta\nu^2 = \Delta\nu_p^2 + \Delta\nu_d^2 + \Delta\nu_l^2$ permits a fit of ν^2 as a function of P^2 . From this analysis, we have the curve drawn in Fig. 4 and a $\Delta\nu_p/P$ of 8 MHz/Torr which is in the anticipated range. While many times the statistical uncertainty, we assess a probable error for this result of ± 3 MHz/Torr, based largely upon the limited pressure range, given the other linewidth contributions. The fitted intercept of 58 MHz is consistent with the expected contributions from Doppler and laser linewidth broadening.

CHEMISTRY

The nonequilibrium physical and chemical conditions that exist in a glow discharge³⁸ frustrate any complete analysis of transient molecule formation, as here for KH. In studies of molecular ions,^{39,54–56} consideration of the initial steps in ion formation have, at least, helped to guide successful gas mixture strategies from both a synthetic and a dynamic point of view. With ions, however, one is aided by the tremendous wealth of knowledge available on their gas phase chemistry and kinetics.^{57–60} Such detailed and well defined support for the chemistry of transient neutral metals unfortunately does not exist. In spite of the nonideal environment and, indeed, because so little is known about the governing chemistry, we point to those processes which we think are the most important in producing KH in the glow discharge, and we support our conjecture with a steady state model of the kinetically limited chemistry of KH. Hopefully this will more clearly call attention to the need for the key kinetic studies.

In our analysis we resort entirely to analogy regarding chemical synthesis and to order of magnitude estimates for reaction cross sections and rate constants. While there has been an interesting study⁶¹ of H_2 reacting with a liquid potassium jet to form solid KH, we focus solely upon a gas phase synthesis, because of the density modulation spectra discussed above and because in previous work¹⁷ it was shown that K atoms lead to KH through gas phase process in an H_2 discharge.

After reflection upon what is already known about the reactions of metal atoms with H_2 , wherein either one or the other is excited (e.g., for Hg^{62–65} and for Cs and Na^{35,66,67}), two KH formation reactions seem to us of greatest importance here:



and



[These reactions are written out separately, yet clearly they are connected, as Eq. (1b) is the reverse of Eq. (2b). Actually, the reactants and the products may more succinctly be thought of as the dissociation products of $(KH_2)^*$.] Excitation in the reactants is required to overcome the unfavorable endothermicity of the purely ground state process (~ 60 kcal/mol⁶⁸). In K^* , this means promotion of the 4s electron to the 3d level, or higher,⁶⁹ and in H_2 , vibrational excitation to $v \geq 6$. The production of K^* in a glow discharge is largely by electron impact



with a cross section of $\sim 2 \times 10^{-14}$ cm².³⁸ Loss of K^* , here, is by the quenching reaction 1 and by radiative emission



A typical lifetime τ_4 should be ~ 40 – 100 ns, as in the reactive 3d and 4d ²D states.⁷⁰ The formation of $H_2(v^*)$ in glow discharges has been experimentally investigated by Shirley and Hall⁷¹ and theoretically analyzed by Capitelli and Molinari.⁷² By appealing to the latter very detailed study, we estimate that $n_{H_2(v^*)} \sim 10^{14}$ cm⁻³ under our conditions (plasma density $\sim 10^{11}$ cm⁻³, density reduced electric field ~ 3 – 4×10^{-16} V cm², and time scale $\sim 10^{-3}$ s). Indeed, excitation of $v = 4$ – 12 is expected to be nearly the same, according to theory. The principle reactions involved are electron impact excitation of H_2 ⁷³ and vibrational energy loss in collisions with ground state H_2 (V–V and V–T).⁷⁴

Balancing the rates of formation and loss for K^* and KH, we have

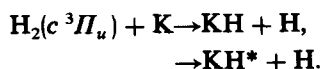
$$n_{K^*} = \frac{\sigma_3 v_e n_e n_K}{k_1 n_{H_2} + 1/\tau_4}$$

and

$$n_{KH} = \frac{k_{1a} n_{K^*} n_{H_2} + k_{2a} n_K n_{H_2(v^*)}}{1/\tau_w},$$

where v_e is the mean electron velocity ($\sim 10^8$ cm/s), n_e is the electron density (here $\sim 10^{11}$ cm⁻³), and n_{H_2} is the H_2 density ($\sim 7 \times 10^{16}$ cm⁻³). An estimated wall temperature of 400 K gives an n_K of 2×10^{12} cm⁻³ from standard tables.⁷⁵ For an estimate of k_{1a} we appeal to an analogy with excited Hg by taking the product of the collision cross section for quenching of Hg* radiation by H_2 (6.01 \AA^2 ⁶³) and the corresponding theoretical branching ratio of HgH to $H_2(v^*)$ of $(0.16/0.59)$,⁶⁵ along with the relative velocity of K and H_2 at 510 K to give 4×10^{-11} cm³ s⁻¹. We have no analogy to appeal to for k_{2a} , so we make the crude assumption that it is equal to k_{1a} . So for K^* , we have $n_{K^*} = 1 \times 10^{10}$ cm⁻³. With all of the factors now evaluated, the density of KH comes out as 6×10^{12} cm⁻³. This close agreement with the measured value of 4×10^{12} cm⁻³ is, of course, partially fortuitous because of the numerical approximations made here, any of which could be off by a factor of 2–5, if not more. Also, we have neglected several intermediate processes that together could contribute as much as those above. A notable one is the

synergistic effect in the loss of H_2 (ν^*) and K^* , as through reactions (1) and (2) they lead to each other. Also neglected is the possibility that electronically excited metastable H_2 molecules (in the $c^3\Pi_u$ state, which has a lifetime of ~ 1 ms⁷⁶) may have sufficient density to produce KH and even KH^* (A state) by



DISCUSSION

With regard to the experimental method used here, clearly it works quite well for KH and could be extended to the other alkali hydrides, providing their chemistry is as favorable. Further infrared work on KH is needed, of course, to improve the band coverage and line position accuracy and to obtain the K-39 and K-41 isotopes of KD. A complete spectrum for the four isotopes would provide an excellent data base for an assessment of Born–Oppenheimer breakdown. In Table III, selected molecular constants are compared with previous results and one can see the improvement obtained from the directly observed infrared spectrum. While the agreement with the pseudopotential MCSCF calculation is extremely good, Stevens has pointed out to us that other alkali hydrides in their study did not fare as well³ and that caution should be exercised in the comparison. Our Y_{10} is compared with ω_e values from the previous work, which is, of course, the correct pairing. The actual ω_e , however, differs from both our Y_{10} and the previous ω_e 's by the Dunham correction

$$Y_{10} = \omega_e(1 + (B_e/2\omega_e)^2 \beta_{10}),$$

where β_{10} can be evaluated by a formula in Dunham's original paper.⁴⁸ Employing the constants from Table II to compute the correction, we obtain $\omega_e = 986.0505(30)$ cm⁻¹. The other Dunham coefficients are not determined with sufficient accuracy to necessitate similar corrections, and thus they can be directly interpreted as B_e , D_e , etc., as usual.

Left in the form given in Table II, the derived constants do not immediately tell us how much has been learned about the potential energy function that governs the motion of the potassium and hydrogen nuclei $U(r)$. By appealing to the usual perturbation treatment,⁷⁷ the equilibrium constants

can be recast in terms of the potential derivatives from the expansion

$$U(r) = U^0|_{r=r_e} + \frac{1}{2} \left. \frac{\partial^2 U}{\partial r^2} \right|_{r=r_e} (r-r_e)^2 \\ + \frac{1}{3!} \left. \frac{\partial^3 U}{\partial r^3} \right|_{r=r_e} (r-r_e)^3 \\ + \frac{1}{4!} \left. \frac{\partial^4 U}{\partial r^4} \right|_{r=r_e} (r-r_e)^4 + \dots$$

From ω_e , $\omega_e x_e$, B_e , and α_e , we find that

$$\left. \frac{\partial^2 U}{\partial r^2} \right|_{r=r_e} = 0.562\,35(2) \times 10^5 \text{ erg cm}^2, \\ \left. \frac{\partial^3 U}{\partial r^3} \right|_{r=r_e} = -1.6566(60) \times 10^{13} \text{ erg cm}^{-3},$$

and

$$\left. \frac{\partial^4 U}{\partial r^4} \right|_{r=r_e} = 4.227(60) \times 10^{21} \text{ erg cm}^{-4},$$

(where the uncertainties reflect only propagated error). Notable is the magnitude of these constants, in that these three contributions fall off at only 20:5:1 at the $\nu = 1$ classical turning point. Also of note is the rather small size of the second derivative in terms of chemical units 0.562 35 mdyne/Å. The other alkali hydrides exhibit small force constants (0.47, 0.52, 0.56, 0.78, and 1.03 mdyne/Å, for CsH to LiH,⁷⁸ which are an order of magnitude smaller than those for the related halogen hydrides HI to HF (3.1, 4.1, 5.3, and 10.1 mdyne/Å.⁷⁸) With respect to the general range of stretching force constants, KH represents a midpoint in known molecular values, in being ~ 40 times smaller than the stiff triple bond force constant in N_2 ⁷⁸ and in being ~ 50 times stronger than the bonds in van der Waals molecules like Ar·HCl.^{79,80} Assuming an energy reference of $U(r = \infty) = 0$, $-U^0|_{r=r_e}$ represents the equilibrium dissociation energy which can be estimated by the Morse potential relation⁸¹

$$U^0|_{r=r_e} = \frac{-hc\omega_e^2}{4\omega_e x_e}.$$

The estimate of -3.2×10^{-12} erg, or a dissociation energy of 2.0 eV, is within 10% of previously reported results (2.11 ± 0.19 eV from a Birge-Spencer plot,¹⁶ 2.06 ± 0.16 eV

TABLE III. Comparison of molecular constants for ³⁹KH (in cm⁻¹).

	ω_e	$\omega_e x_e$	B_e	α_e	D_e	$r_e(\text{\AA})$
Present work ^a	985.6714(80)	14.90 13(10)	3.416 40(10)	0.085 313(26)	1.6354(36)	2.241 152(16)
Yang, <i>et al.</i> ^b	985.24(40)	14.92(20) ^b	3.412 6(17)	0.081 6(28)	...	2.242 4(16)
Giroud and Nedelec ^{c,s}	985.38	15.08 ^d	3.415	0.081	1.53	2.242
Bartky ^f	983.63(57)	14.32(10)	3.412 3(13)	0.0817(10)	...	2.24
Stevens, <i>et al.</i> ^e	985.7	14.6	2.24

^a $\omega_e \approx Y_{10}$, $B_e \approx Y_{01}$, $D_e \approx Y_{02}$, $r_e = (16.8580/\mu(\text{amu})/Y_{01}(\text{cm}^{-1}))^{1/2}$.

^b $\omega_e y_e = 0.088(28)$ cm⁻¹, which we cannot determine here, as this requires observation of another vibrational level.

^c No error limits given.

^d $\omega_e y_e = 0.1$ cm⁻¹ and $\omega_e z_e = -0.0022$ cm⁻¹.

^e Reference 3.

^f Reference 14.

^g Reference 16.

^h Reference 26.

from mass spectroscopic studies,⁸² 1.86 ± 0.05 eV from an RKR and avoided crossing potential curve analysis,⁸³ and a theoretical, pseudopotential value of 1.80 eV.³ While in general one does not expect the Morse formula to work this well, inspection of many closed shell hydride cases⁸ shows an accuracy of 10%–20%. Taken altogether then, the high resolution infrared spectrum has led to a fairly strong characterization of the potential function $U(r)$ for KH.

Measurement of the linewidths and the effects of pressure broadening of KH by H₂ is most interesting because of the anticipated high polarity of KH and the resulting enhanced pressure broadening cross section through the dominating dipole-quadrupole interaction. The pressure broadening coefficient of 8 ± 3 MHz/Torr found here is in the range 5–9 MHz/Torr expected at 510 K. Clearly, more detailed measurements over a greater pressure range are needed to verify this result. One particularly interesting point to follow up will be the dependence upon the rotational state of KH, as the quasiresonant theory⁵² suggests no such dependence when the dipole-quadrupole interaction dominates. In related HCl-H₂ broadening experiments,⁸⁴ there is a marked rotational dependence. The polarity of HCl is, however, much less (1 vs 7 D) and thus other long range interactions come into play.^{5,86} A related investigation that would be most helpful in understanding KH pressure broadening is an evaluation of the dipole moment of KH either by experimental means (e.g., electric resonance) or by accurate theoretical calculation.

The agreement of our rough, order-of-magnitude KH density calculation with the measured density points to the importance of the two reactions which we feel are responsible for KH production. Clearly, gas phase kinetic studies of these reactions are highly desirable, not only to help understand our observations here, but also to understand the other experiments involving excited alkali metal atoms and molecular hydrogen referred to earlier. This especially pertains to Happer and co-workers' laser induced nucleation studies,^{35,36} considering the potential for laser controlled isotope separation of metal atoms by their excited state chemistry with H₂. Our simple chemical model also suggests a very interesting theoretical study that would be valuable, namely, a calculation of the potential surfaces for Rydberg states of (KH₂)*, which would represent the reactive surfaces for reactions (1) and (2). The current development of pseudopotential calculations at the multiconfiguration level³ indicates that they may be particularly well suited to this task, and in view of the total lack of experimental kinetic information, the theoretical results would be most welcome.

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