The Pure Rotational Spectra of $^{84}KrH^+$ and $^{86}KrH^+$ [1]

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Rotational absorption spectra of the krypton hydride ion in its ground electronic and vibrational state have been measured with tunable far-infrared radiation. These accurate frequency measurements determine the rotational constants B, D, and H, and yield transition frequencies accurate to 40 kHz (1σ). By combining the new results with the former microwave data on several isotopic forms of $^xKrD^+$ a Dunham analysis can be performed, yielding accurate information on the Born–Oppenheimer breakdown parameters.   © 1997 Academic Press

INTRODUCTION

The absorption ground state spectra of several protonated rare gas molecules have been reported in past years (1–10). Most of these observations concern either relatively low-resolution infrared data (e.g., HeH^+ (1), NeH^+ (2), and XeH^+ (8)) or high-resolution microwave data for different isotopes, but only for the lowest rotational transition (e.g., ArD^+ (3), KrD^+ (5), and XeH^+/XeD^+ (10)). The best way to study the rotational progression, however, is to use tunable far-infrared (TuFIR) radiation, since the rotational constants for these types of ions are typically in the range of 8 to 15 cm^{-1}. This was shown previously for ArH^+ only (7). Here we report the observation of the pure rotational transitions of $^{84}KrH^+$ and $^{86}KrH^+$ in their ground vibrational states.

The transition frequencies of both $^{84}KrH^+$ and $^{86}KrH^+$ can be calculated rather accurately with the Dunham coefficients obtained from the infrared emission work of Johns (4) and the microwave work of Warner et al. (5). In 1992 the electric dipole moment was studied experimentally by Linnartz et al. (11) using a magnetically extended anomalous discharge, measuring the isotopic dependence of the rotational g-factor by looking at the difference in Zeeman splittings for the $J = 1 \leftarrow 0$ $^{84}KrH^+$ and $J = 2 \leftarrow 1$ $^{84}KrD^+$ transitions. A major influence of the zero point vibrations, however, did not allow for a direct comparison with the theoretically predicted value of the electric dipole moment of 1.944 D by Rosmus and Reinsch (12).

EXPERIMENTAL

In our experimental setup, coherent far-infrared radiation is generated in a metal–insulator–metal (MIM) diode using a tunable sideband of microwave radiation on the difference frequency of two CO_2 lasers (13). The far-infrared radiation is detected with a gallium-doped germanium bolometer, cooled to the lambda point of ^4He. Since several transitions coincide with strong water absorptions it is necessary to flush the far-infrared path between the MIM diode and the detector with dry air. The KrH^+ ions are generated in a hollow cathode discharge similar to that described in (14). The tube is about 1 m long and has an inner diameter of 32 mm. During the experiment it is liquid nitrogen cooled. For the generation of both $^{84}KrH^+$ and $^{86}KrH^+$, a mixture of Kr (with natural abundances of 56.9% ^{84}Kr and 17.4% ^{86}Kr) and H_2 in a ratio of about 20 to 1 is used at a pressure of 106 Pa (800 mTorr) with a discharge current of about 300 mA. No signals were found at lower pressures. The mixture differs from the optimal conditions that were found for the anomalous discharge, where the Kr:H_2 ratio was 1:4. However, as in (11), the H_2 dependence was not very critical in our experiment. This is clearly different for HeH^+ (1) and ArH^+ ($7, 15$), where too much H_2 immediately quenches the signal and typical mixing ratios for rare gas to H_2 of $10^2/10^4$:1 are used. This is probably due to the greater proton affinity of Kr which partly compensates for losses in the form of $RgH^+ + H_2 \rightarrow Rg + H_3^+$.

RESULTS

We have recorded seven transitions for $^{84}KrH^+$ and six for $^{86}KrH^+$. The $^{86}KrH^+$ $1 \leftarrow 0$ transition is missing because of a poor signal-to-noise ratio. The measured frequencies together with the experimental uncertainties are listed in Table 1. In Fig. 1 a typical first-derivative signal of the $J = 4 \leftarrow 3$ transition of $^{86}KrH^+$ is shown. The frequencies are determined using a line-fitting program and averaging the results of several scans.

TABLE 1
The Rotational Transitions in the Ground Vibrational State of ^{84}KrH$^+$ and ^{86}KrH$^+$
(All Values Are Given in MHz)

J′←J″ ^{84}KrH$^+$	Observed ν	Obs.-Calc.[1]	Obs.-Calc.[2]
1 ← 0	494 515.29(10)	0.09	- 0.68
2 ← 1	988 760.25(10)	0.14	- 1.31
3 ← 2	1 482 464.56(04)	- 0.04	- 1.98
4 ← 3	1 975 358.85(14)	0.01	- 2.18
5 ← 4	2 467 173.55(10)	0.12	- 2.07
6 ← 5	2 957 639.56(06)	- 0.02	- 1.98
7 ← 6	3 446 489.29(16)	0.03	- 1.54

J′←J″ ^{86}KrH$^+$	Observed ν	Obs.-Calc.[1]	Obs.-Calc.[2]
1 ← 0	(494 379.78)[3]		
2 ← 1	988 489.42(04)	0.01	- 1.41
3 ← 2	1 482 058.82(19)	- 0.08	- 2.01
4 ← 3	1 974 818.50(20)	- 0.06	- 2.28
5 ← 4	2 466 499.15(09)	0.00	- 2.28
6 ← 5	2 956 832.06(10)	0.02	- 2.10
7 ← 6	3 445 549.33(15)	- 0.01	- 1.83

[1] Calculated value obtained using the derived parameters from Table II.

[2] Calculated value from the Dunham coefficients determined in [4, 5].

[3] Calculated value using the constants listed in Table II.

ANALYSIS AND DISCUSSION

Using the standard way to describe the frequency of pure rotational transitions in a $^1\Sigma$ state, the rotational and centrifugal distortion constants B, D, and H, defined in Eq. [1], are determined. No relevant physical parameter could be determined for the octic centrifugal distortion parameter L. The recorded transitions are fitted to

$$\nu = 2B(J + 1) - 4D(J + 1)^3 \\ + 6H(J + 1)^3[(J + 1)^2 + \tfrac{1}{3}] + \cdots \quad [1]$$

and each measurement is weighted inversely as the square of the estimated uncertainty, yielding the constants as listed in Table 2. The difference between observed and calculated frequencies is listed in Table 1 as well. The quality of the least-squares fit is of the same order as or better than the estimated experimental uncertainty.

In order to compare the results with the predictions from the Dunham coefficients, obtained by Johns (4) and extended for the Born–Oppenheimer breakdown parameters Δ_{01}^{Kr} and Δ_{01}^{H} by Warner *et al.* (5), the rotational energy levels for $v = 0$ are calculated according to

$$E_{0J} = \Sigma_{kl}Y_{kl}(\tfrac{1}{2})^k[J(J + 1)]^l \quad [2]$$

where Y_{kl} is given in terms of mass independent parameters by

$$Y_{kl} = \mu^{-(k/2+l)}U_{kl}\left[1 + m_e\frac{\Delta_{kl}^a}{M_a} + m_e\frac{\Delta_{kl}^b}{M_b} \right]. \quad [3]$$
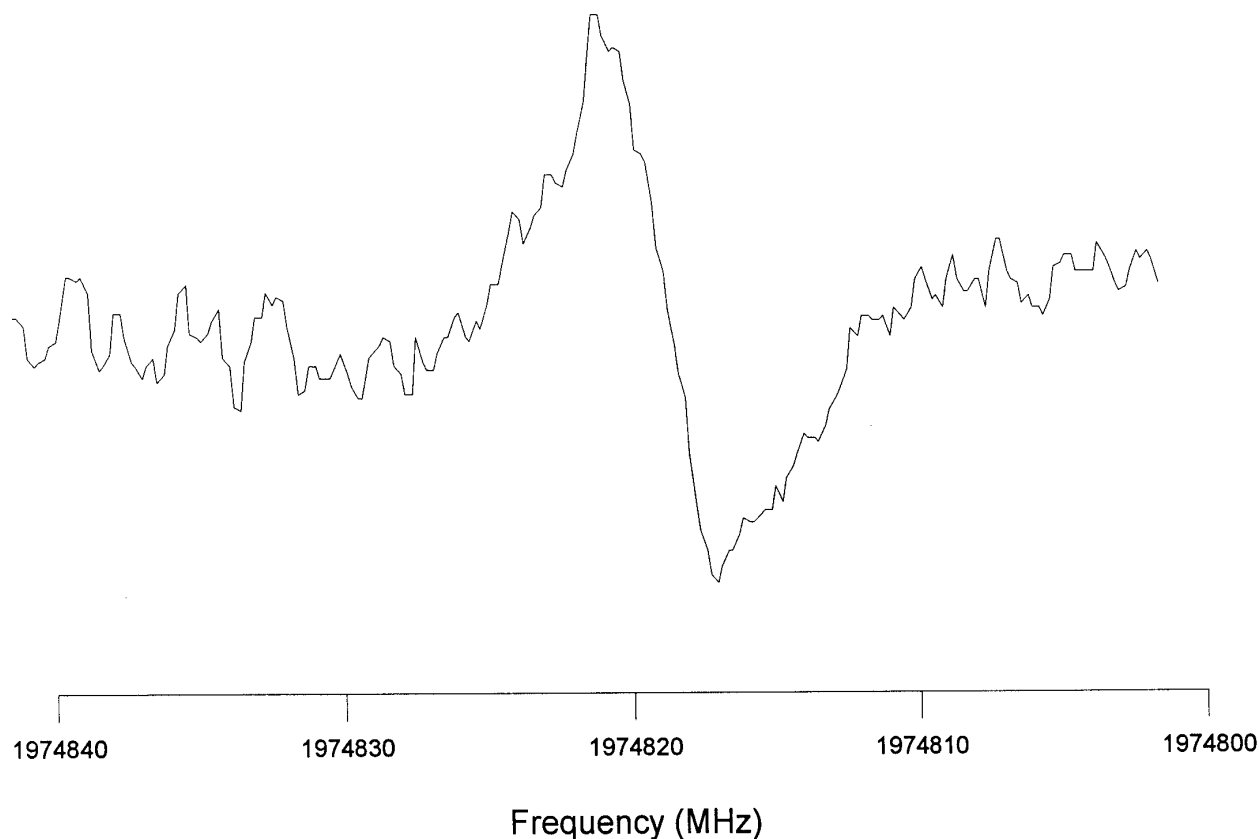
FIG. 1. The $J = 4 \leftarrow 3$ rotational transition of $^{86}\text{KrH}^+$ in its ground vibrational state.

Here μ is the charge-adjusted reduced mass and m_e the electron mass. For the constants the values as listed in (5) are used. It turned out to be necessary to include also the U_{03} and U_{04} terms for the higher rotational transitions. As was assumed by Warner *et al.* (5) only the Δ_{01} parameters will have a nonnegligible effect and consequently no higher terms are considered here.

In the last column of Table 1 the deviation of the observed

TABLE 2
Ground State Constants (in MHz) for $^{84}\text{KrH}^+$ and $^{86}\text{KrH}^+$

	$^{84}\text{KrH}^+$	$^{86}\text{KrH}^+$
B	247 280.125 (15)	247 212.404 (4)
D	11.2635 (7)	11.2578 (2)
10^3 H	0.2075 (87)	0.2101 (24)

Note. The figures in parentheses represent one standard deviation of the least-squares fit, in units of the last quoted decimal place.

frequencies minus the frequencies predicted from the Dunham coefficients is shown. Although this value is small—with less than 2.3 MHz it shows the quality of the work presented in (4, 5)—it systematically exceeds the observed data. Since the deviation decreases for higher J levels it is unlikely that this is caused by missing higher U_{kl}'s. Therefore we suggest that the values obtained for the Born–Oppenheimer set—U_{01}, Δ_{01}^{Kr}, and Δ_{01}^{H}—from the $J:1 \leftarrow 0$ $^x\text{KrD}^+$ transitions may be too inaccurate to get an even better agreement. This may also be concluded from the fact that the $^{84}\text{KrH}^+$ measurements presented here yield a slightly lower $(U_{01})_{\text{eff}}$ of 250 231.74(25) MHz, compared to the result found in (4, 5). Unfortunately, the ultimate accuracy with which the Born–Oppenheimer parameter set can be obtained is determined mainly by the number of isotopes investigated, and not by the number of transitions observed per isotope. For this reason the new data for $^{84}\text{KrH}^+$ and $^{86}\text{KrH}^+$ alone are not sufficient to obtain more accurate constants. However, by combining these results with the data available from (5) for the deuterated species, a further analysis can be performed. Following the same method as used in (5, 10), the averaged $^{84}\text{KrH}^+$ and $^{86}\text{KrH}^+$ results are plotted graphically as a function of M_{Kr}^{-1}. A linear least-squares fit yields $U_{01}(1 + m_e(\Delta_{01}^{\text{H}}/M_{\text{H}}))$ and $U_{01}m_e\Delta_{01}^{\text{Kr}}$ for the intercept and slope of

TABLE 3
The Dunham Coefficients for KrH$^+$ (U_{kl}'s Are in MHz)

Quantity	Value[1]	Value[2]
U_{01}	250 214.66(15)	250 214.364(300)
$(U_{01})_{eff}$	250 231.74(25)	250 232.03(30)
$U_{01}(1+m_e\frac{\Delta_{01}^H}{M_H})$	250 222.646(15)	
Δ_{01}^{Kr}	0.682(70)	0.682(70)
Δ_{01}^{H}	0.1172(20)	0.1215(40)
$r_e^{BO}(\text{Å})$	1.421 1904(5)	1.421 1911(7)

[1] This work.

[2] Reference [5].

the fit, respectively. As a constraint the slope must be the same as that found for the ^{x}KrD$^+$ results. With the resulting set of equations the constants as listed in Table 3 can be calculated. The value for Δ_{01}^{Kr} stays nearly the same, as may be expected. The value for Δ_{01}^{H} shifts, but still within the error limits compared to the value found in (5). The error in Δ_{01}^{Kr} is determined by the precision of the ^{x}KrD$^+$ measurements and, consequently, does not improve here. The error in Δ_{01}^{H} and U_{01}, however, can be decreased. Since the determination of these constants does not depend anymore on the infrared data, as was necessary in (5), but on high-resolution TuFIR results, higher accuracies can be obtained. With the new set a better prediction for $(U_{01})_{eff}$ can be made, which indeed partly corrects for the (small) systematic deviation found for the old constants. Finally, from the value of U_{01} the Born–Oppenheimer bond distance can be calculated using the relation (10)

$$U_{01}(r_e^{BO})^2 = 505\ 379.074\ \text{MHz amu Å}^2,$$

yielding $r_e = 1.4211904(5)$ Å. This value is in good agreement with the theoretically predicted value of 1.419(3) Å (12). The error is determined mainly by the experimental precision with which U_{01} can be calculated.

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