

Determination of the Electric Dipole Moment of KrH^+

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By measuring the isotope shifts of the rotational g_{R} -factors of different isotopic species the electric dipole moment of the molecular ion KrH^+ was determined. For that purpose we studied the Zeeman effect of the $J = 1 \leftarrow 0$ transition of KrH^+ at 494.5 GHz and the $J = 2 \leftarrow 1$ transition of KrD^+ at 503 GHz. In a magnetic field of 4.950 T the rotational transition splits into two $\Delta M = \pm 1$ components, resulting in splittings of approximately 41.8 MHz (KrH^+) and 21.1 MHz (KrD^+). It turned out that there is a major influence of the zero-point vibrations on the experimentally determined electric dipole moment, which results in an uncertainty of the interpretation of the experimental data. The ions were generated in a modified anomalous discharge placed in a superconducting magnet. The transitions were observed by direct absorption of the harmonics of a 70-GHz klystron, using the tunable FIR sideband spectrometer at Nijmegen university.

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1. INTRODUCTION

Determination of the electric dipole moment of molecular ions by conventional Stark spectroscopy, as is usual for neutral molecules, is not possible, because the electric field accelerates the ions towards the wall of the discharge tube. However, the electric dipole moment of molecular ions in a $^1\Sigma$ state can be determined by measuring the Zeeman splitting for several isotopes and by determining the isotope shift of the rotational g factors. Townes *et al.* (1) showed that when zero-point vibrations are neglected, knowledge of the experimentally determinable rotational magnetic g_{R} factor for two different isotopic species allows the calculation of the electric dipole moment, using the expression

$$\boldsymbol{\mu} \cdot \mathbf{d} = -\frac{eh}{16\pi^2 M_{\text{p}}} \left(\frac{g'_{\text{R}}}{B'} - \frac{g_{\text{R}}}{B} \right) + \frac{1}{2} Qe|\mathbf{d}|^2 \quad (1)$$

Here $\boldsymbol{\mu}$ is the electric dipole moment, \mathbf{d} the displacement vector of the center of mass of the primed isotopic species referred to the center of mass of the nonprimed isotopic species, g_{R} the rotational g factor, B the rotational constant, and Q is the net charge of the ion. Because g_{R}/B and g'_{R}/B' represent two nearly equal quantities, it is necessary

radiation is frequency modulated at 5 kHz and the detector output is monitored at twice this frequency at a PDP11/23+ computer using a phase-sensitive detector.

The ions were generated in a liquid-nitrogen-cooled discharge cell using a mixture of Kr and H₂ (D₂). In order to increase the signal strength at low pressures (typically less than 50 mTorr, therefore pressure broadening is almost suppressed), a magnetically enhanced anomalous glow discharge is used (11). In order to allow measurements at a high magnetic field, which is both used for the extension of the negative glow as for the Zeeman field, we have chosen a modified cathode design, starting with the setup described in Ref. (3): An adjustable stainless steel cathode surface was used to keep the discharge voltage sufficiently high. For that purpose the cathode surface can be altered by sliding a glass tube inside the cathode. Maximum signal-to-noise ratios were achieved with an uncovered cathode length of about 2 cm, which yielded a discharge current of 5 mA at a voltage of 1.6 kV. However, after half an hour the discharge became instable, which turned out to be the result of the sputtering of the stainless steel on the tube. The resulting metal layer on the inner glass tube increased the cathode surface, thereby changing the discharge conditions substantially. Therefore we tried a 1-cm long stainless steel cathode, without glass tube, which turned out to be a good alternative (Fig. 2). Normal discharge conditions were 4 mA at 1 kV. Signals of the isotopic species KrH⁺ and KrD⁺ were generated with a mixture of Kr and H₂ or D₂ in a ratio of about 1:4.

3. RESULTS

Direct absorption spectroscopy of molecular ions in the far infrared frequency range is usually performed with the use of a hollow-cathode discharge cell (12) or a cell with a magnetically extended negative glow. To determine the production efficiency we have first tried to detect KrH⁺ and KrD⁺ in the hollow-cathode discharge (Fig. 3). The transition frequencies can be very accurately calculated with the Dunham coefficients obtained from infrared emission (8) and microwave work (9). The measured frequencies agree within 1 or 2 MHz with the calculated ones.

The transitions of KrH⁺ ($J = 1 \leftarrow 0$) and KrD⁺ ($J = 2 \leftarrow 1$) around 500 GHz were detected using the harmonics of a 70-GHz klystron. The frequencies around 1500 GHz were generated using the first sideband of an 80-GHz klystron and the

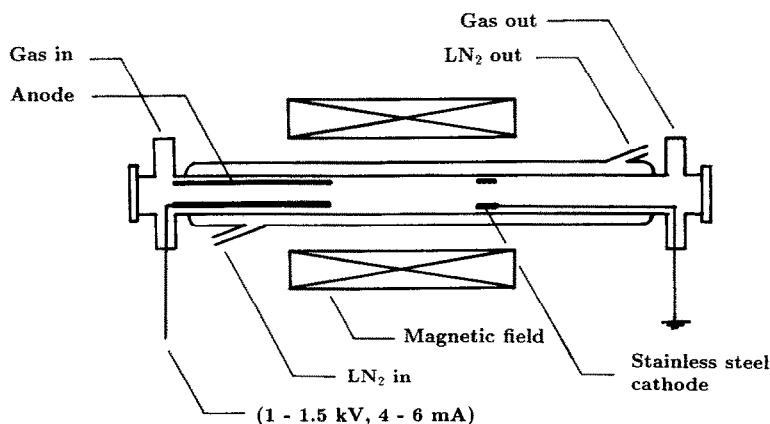


FIG. 2. The modified discharge for measurements in high magnetic fields with a small fixed cathode surface in order to circumvent sputtering problems.

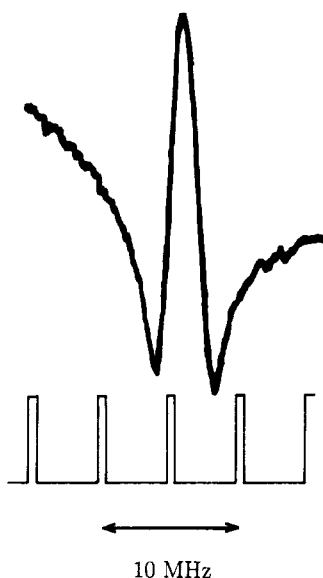


FIG. 3. Recording of the $J = 1 \leftarrow 0$ transition of $^{84}\text{KrH}^+$ in the hollow-cathode discharge.

9R(34) CO_2 -laser pumped CH_2F_2 FIR-line at 1 397 118.6 MHz. Unfortunately it is not possible to measure the $J = 3 \leftarrow 2$ of $^{84,86}\text{KrD}^+$ at 754 GHz, due to strong H_2O absorption centered at 752 GHz. The same holds for the $J = 2 \leftarrow 1$ of $^{84,86}\text{KrH}^+$ at 988.8 GHz, due to strong absorption around 987.8 GHz (13). The KrH^+ $J = 3 \leftarrow 2$ transition at 1482 GHz is very strong, even stronger than transitions of the well known "strong absorbers" N_2H^+ and HCO^+ . The KrH^+ $J = 1 \leftarrow 0$ transition is weaker. Assuming Doppler broadening and a rotational temperature of 150 K, the calculated ratio of the peak absorptions at 1500 and 500 GHz is approximately 5. However, from an experimental point of view it is easier to perform the dipole measurements on the 500-GHz transitions, because the frequencies of both KrH^+ and KrD^+ can be generated with the harmonics of one single klystron. This has the advantage that the frequency can be determined more precisely, since no FIR laser is involved. Furthermore, Doppler broadening is increased by a factor of three at 1500 GHz, which increases the error in the frequency.

The Zeeman splittings of the $J = 1 \leftarrow 0$ transition of $^{84}\text{KrH}^+$ and the $J = 2 \leftarrow 1$ transition of $^{84}\text{KrD}^+$ were recorded in a magnetic field of 4.950 T, using an anomalous discharge. The measured transitions are shown in Figs. 4 and 5. The spectra have been recorded by computer, and a curve fitting with 500 points per line was carried out. Each Zeeman component was fitted with a Gaussian profile determined by three parameters: the height, the transition frequency, and the width of the line. The result of the curve fits is also shown in these figures. The SNR of the KrH^+ lines turns out to be an order of magnitude smaller than that of the KrD^+ . This is probably due to a worsening of the discharge conditions during our measurements. The results from two successive scans of the same isotopic species deviated by less than 25 kHz for the KrD^+ and by less than 100 kHz for the KrH^+ . The results are listed in Table I.

4. THEORY

The Zeeman energy for a linear $^1\Sigma$ molecule is given by $E = g_{\text{R}}\beta_{\text{I}}M_JH$ (H magnetic field, β_{I} nuclear magneton). In a magnetic field perpendicular to the polarization of

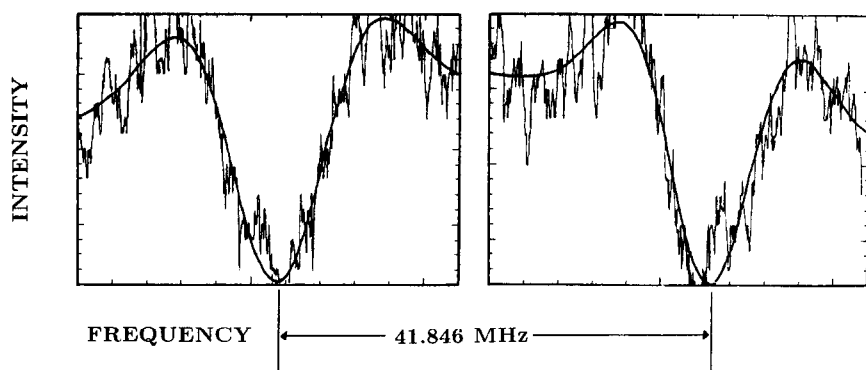
SPLITTING OF KRH⁺

FIG. 4. The experimental and fitted line splitting for the $^{84}\text{KrH}^+$ ($J = 1 \leftarrow 0$) transition in a magnetic field of 4.950 T.

the laser, pure rotational transitions split as $\nu = \nu_0 \pm \beta_I g_R H$, where ν_0 is the zero-field transition and the \pm corresponds to allowed $\Delta M = \pm 1$ transitions. This means that two separate transitions can be observed, split by $\Delta\nu = 2g_R\beta_I H$.

If the same magnetic field is used for measurements on two isotopically substituted species, Eq. (1) can be modified to

$$\mu = -\frac{eh}{16\pi^2 M_p \Delta z} \frac{1}{2\beta_I H} \left(\frac{\Delta\nu'}{B'} - \frac{\Delta\nu}{B} \right) + \frac{1}{2} Qe\Delta z, \quad (2)$$

with Δz being the shift in the center of mass upon isotopic substitution ($z' = z - \Delta z$) and with $\Delta\nu$ and $\Delta\nu'$ the Zeeman splittings for the two species.

The application of this formula is based on the assumption that the structure of the molecule remains constant upon isotopic substitution. This implies that only the

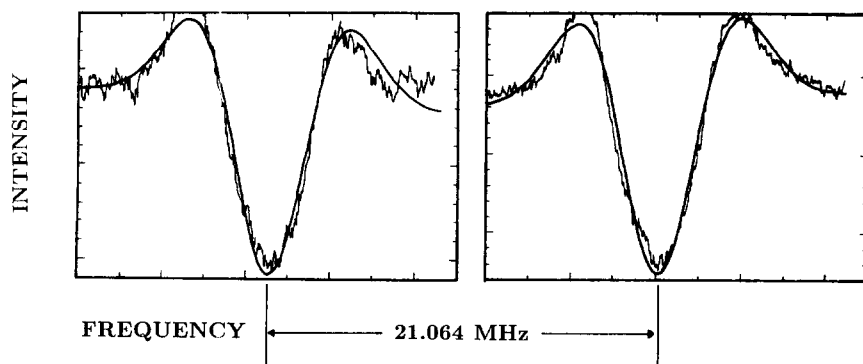
SPLITTING OF KRd⁺

FIG. 5. The experimental and fitted line splitting for the $^{84}\text{Krd}^+$ ($J = 2 \leftarrow 1$) transition in a magnetic field of 4.950 T.

TABLE I

The Zeeman Splittings at 4.950 T for ⁸⁴KrH⁺ and ⁸⁴KrD⁺, with Resulting Experimental *g_R* Factors

| Ion | Component | Frequency | Splitting | <i>g_R</i> |
|--------------------------------|-----------|-------------|-----------|----------------------|
| ⁸⁴ KrD ⁺ | Low | 503010.7580 | → 21.064 | - 0.279113 |
| | High | 503031.8215 | | |
| ⁸⁴ KrH ⁺ | Low | 494494.452 | → 41.846 | - 0.554489 |
| | High | 494536.298 | | |

center of mass is shifted, while the distance between the atoms is kept constant. An internuclear distance $r_{\text{KrH}^+} = 1.42 \text{ \AA}$ (7, 9) leads to a value for the shift in the center of mass of Δz (⁸⁴KrH⁺ → ⁸⁴KrD⁺) = 0.0163 Å. However, this is only partly true, mainly due to the effects of zero-point vibrations, which are different for distinct isotopic configurations. This zero-point vibration causes the vibrationally averaged *r*-value (*r*₀), being the distance between the atoms, to deviate from *r*_e. The experimentally determined Zeeman splitting will yield *g*(*r*₀) rather than *g*(*r*_e). It was therefore tried in the ArH⁺ measurements (2) to extrapolate the *g_R* factor for both isotopes to *r*_e and by subsequent use of Eq. (2) to determine $\mu(r_e)$. In the N₂H⁺ experiment (3) this procedure was not necessary because the “heavy” N-atom was substituted so that the influence of zero-point vibrations are indeed negligible. For KrH⁺/KrD⁺ as well as for ArH⁺/ArD⁺ this is not the case. In order to circumvent this problem we also tried to substitute the heavy component. Therefore we measured the splitting for ⁸⁶KrD⁺ but the accuracy that could be achieved in determining the line positions together with the very small value of Δz (⁸⁴KrD⁺ → ⁸⁶KrD⁺) was not sufficient to yield a significant value for μ . We have followed an alternative approach to deduce the vibrational equations.

The rotational *g* factor can be expressed as a sum of nuclear and electronic contributions (14),

$$g_R(r) = g_{\text{nuc}} + g_{\text{el}} = \frac{M_p}{I(r)} \sum_k Z_k z_k^2 - \frac{2M_p}{mI(r)} \sum_{n \neq 0} \frac{|\langle n | L_x | 0 \rangle|^2}{E_n - E_0}, \quad (3)$$

where *M_p* is the proton mass, *m* the electron mass, *Z_k* the charge, and *z_k* the coordinate of nucleus *k*. *L_x* is the electronic angular momentum about the *x*-axis, *E_n* and *E₀* are the energy of the electronically excited state *n* and ground state 0, and *I*(*r*) is the moment of inertia (*m_{red}r*²). From here on we will use unprimed quantities for KrH⁺ and primed quantities for KrD⁺.

While *g_{nuc}* can be shown to be independent of *r*, this is not the case for *g_{el}*. If we assume that $\sum_{n \neq 0} |\langle n | L_x | 0 \rangle|^2 / (E_n - E_0)$ is independent of *r*, *g_{el}* would vary as *I*⁻¹, according to the equation above. This assumption seems reasonable for well separated electronic states, like in KrH⁺, where the sum should be nearly constant for small variations of *r*. Therefore we would expect an *r*-dependence of *g_{el}* as *r*⁻². We then can easily obtain the dipole moment in two limiting cases:

(i) *g_R* dominated by *g_{nuc}*. In this case *g_R* = *g_{nuc}* is independent of *r*. This implies that *g_R*(*r*_e) = *g_R*(*r*₀), where *g_R*(*r*₀) corresponds to the measured quantities. Using this we can determine $\mu(r_e)$ according to

$$\mu(r_e) = -\frac{eh}{16\pi^2 M_p \Delta z} \left(\frac{g'_R(r_e)}{B'_e} - \frac{g_R(r_e)}{B_e} \right) + \frac{1}{2} Qe\Delta z. \quad (4)$$

(ii) g_R dominated by g_{el} . We now have to extrapolate the $g_R (= g_{el})$ values to a common r value, which not necessarily has to coincide with the equilibrium distance r_e , and for convenience we have extrapolated g'_R and g_R to r_0 , the mean r value of KrH^+ at $v = 0$. Therefore the measured g'_R value, $g'_R(r'_0)$, where r'_0 is the mean r value of KrD^+ at $v = 0$ ($r_0 \neq r'_0$), has to be extrapolated to $g'_R(r_0)$. If we assume that $g_{el} \propto r^{-2}$, then

$$g'_R(r_0) = g'_R(r'_0) \left(\frac{r'_0}{r_0} \right)^2 \quad (5)$$

$$B'(r_0) = B'(r'_0) \left(\frac{r'_0}{r_0} \right)^2. \quad (6)$$

This results in

$$\mu(r_0) = -\frac{eh}{16\pi^2 M_p \Delta z} \left(\frac{g'_R(r'_0)}{B'(r'_0)} - \frac{g_R(r_0)}{B(r_0)} \right) + \frac{1}{2} Qe\Delta z, \quad (7)$$

where $(g'_R(r'_0)/B'(r'_0)) = (g'_R(r_0)/B(r_0))$, as can be seen from Eqs. (5) and (6).

If we apply these equations to our data, we obtain in the first case an electric dipole moment of $\mu(r_e) = 1.0$ D. In the second case we find an absolute value for $g'_R(r_0) = g'_R(r'_0)(r'_0/r_0)^2 = 0.2777829$, resulting in a value of $\mu(r_0) = 1.8$ D.

We now describe the case where neither of the two limiting cases is applicable. From Eq. (3) we find that $g_{\text{nuc}}^{\text{KrH}^+} = 0.985555$ and that $g_{\text{nuc}}^{\text{KrD}^+} = 0.494917$. Before we can calculate g_{el} according to $g_{el} = g_R - g_{\text{nuc}}$, we have to know the sign of g_R .

Since \mathbf{d} is pointing in the direction from the hydrogen atom towards the Kr atom, a negative difference of $((g'_R/B') - (g_R/B))$ implies that μ is pointing from H towards Kr (polarity $^+\text{Kr-H}^-$). A positive difference means that μ is pointing from Kr in the direction of H (polarity $^-\text{Kr-H}^+$). Ab initio calculations clearly predict the polarity $^-\text{Kr-H}^+$. By putting in the measured g_R and B values, we see that in this case g_R and g'_R (assuming that they have the same sign) have to be negative. From the calculated values for g_{nuc} we then find the values listed in Table II.

Now g_R can be extrapolated by

$$g'_R(r_0) = g'_{\text{nuc}} + g'_{el}(r'_0) \left(\frac{r'_0}{r_0} \right)^2 \quad (8)$$

if we assume that $\sum_{n \neq 0} |\langle n | L_x | 0 \rangle|^2 / (E_n - E_0)$ is really independent of r ; r_0 and r'_0 were calculated according to the formula $r^2 = 505379 / Bm_{\text{red}}$ MHz \AA^2 amu using the

TABLE II

The Nuclear and Electronic Contribution to the g_R Factor

| Ion | g_R | g_{nuc} | g_{el} |
|------------------|-----------|------------------|----------|
| KrD ⁺ | -0.279113 | 0.494917 | -0.77403 |
| KrH ⁺ | -0.554489 | 0.985555 | -1.54004 |

results of Johns (8). This can also be considered as an approximation. We then obtain a dipole moment of $\mu = 3.0$ D. By different methods of extrapolating the *same* experimental data result in different values for the electric dipole moment, which do not agree within their experimental uncertainty (about 0.3 D). From this we can state that although the experimental accuracy is very good we are not able to obtain a final value for the dipole moment without more information on the r -dependence of $g_{\text{el}}(r)$.

Whereas in the paper of Laughlin *et al.* (2) the correction of μ by extrapolating r is estimated smaller than 0.6 D, we find a much bigger influence on the final value of the dipole moment. It is also intriguing to note that the g_{R} for KrH^+ was found to be negative. We should therefore expect to find also a negative g_{R} value for ArH^+ , but according to Ref. (16), the sign was determined to be positive by comparing ArH^+ with CO, which was found to have an opposite sign for g_{R} , and by using the result that CO has a negative g factor (15). So far we have no explanation for this discrepancy.

4.1. Summary

We found evidence for a major influence of the zero-point vibrations on the experimentally determined dipole moment using the method suggested by Townes *et al.* (1). These influences do not allow us to give a final result for the experimental value of the dipole moment as long as the r -dependence of g_{el} is not exactly known.

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