Determination of the Electric Dipole Moment of KrH+

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By measuring the isotope shifts of the rotational $g$-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 $J = 1 \leftrightarrow 0$ transition of KrH$^+$ at 494.5 GHz and the $J = 2 \leftrightarrow 1$ 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.

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

$$\mu \cdot d = - \frac{e\hbar}{16\pi^2M_p} \left( \frac{g'_R}{B'} - \frac{g_R}{B} \right) + \frac{1}{2} Qe|d|^2$$ (1)

Here $\mu$ is the electric dipole moment, $d$ 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
to measure these ratios with very high precision in order to obtain an acceptable error for $\mu$. The result will be both the value and the sign of the electric dipole moment.

In contrast to a large number of ab initio calculations, there are only two experimentally determined electric dipole moments of molecular ions up to now. The first direct measurement of an electric dipole moment was carried out by Laughlin et al. for ArH$^+$ (2), the second by Havenith et al. for the astrophysically important ion HN$_2^+$ (3). The ArH$^+$ measurement resulted in a dipole moment of $(3.0 \pm 0.6)$ D, whereas a theoretical value of 2.2 D was obtained by Rosmus (4). The dipole moment of HN$_2^+$ was determined as $(3.4 \pm 0.2)$ D, which agreed very well with the theoretical value obtained by Botschwina (5): 3.37 D. Because of these controversial results it seemed worthwhile to perform another measurement. Related to the problematic discrepancy between theory and experiment is the question of whether the zero-point vibrations have to be taken into account. This was the subject of various studies (2, 6) but no satisfying explanation could be found, yet. Therefore, we decided to choose a second rare-gas hydride ion as a further candidate, KrH$^+$, for which high-precision ab initio calculations, done by Rosmus and Reinsch (7), predict an electric dipole moment of 1.944 D. Zero-point vibrations should have a similar impact on the result for this ion as that for ArH$^+$.

In this work, we present the determination of the electric dipole moment of KrH$^+$ and a discussion regarding the influence of the extrapolation of $g_R(r)$ on the value of the dipole moment. Using the Dunham coefficients of Johns (8) and Warner et al. (9) we were able to find some FIR transitions for KrH$^+$ and for KrD$^+$.

2. EXPERIMENTAL DETAILS

In order to keep the error in $g_R$ as small as possible, the Zeeman splittings of pure rotational transitions were measured in high (4.950 T) and highly stable (fluctuations less than 0.05%) magnetic fields. The lines were recorded in the submillimeter region where the linewidth, determined by Doppler and pressure broadening, was sufficiently small. The spectra were recorded with the tunable FIR sideband spectrometer in Nijmegen (10) (Fig. 1). The radiation used for the dipole measurements was generated with the seventh harmonic of a 70-GHz klystron in a Schottky barrier diode and selected using a monochromator with a grating of 0.8 grooves/mm. The radiation passes the discharge cell and is focussed onto an InSb hot-electron bolometer.
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 H$_2$ (D$_2$). 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 unstable, 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 H$_2$ or D$_2$ 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 X0-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.](image)
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$_2$F$_2$ FIR-line at 1397 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$_2$O 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$_2$H$^+$ 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 $E = g_R\beta_I M_J H$ ($H$ magnetic field, $\beta_I$ nuclear magneton). In a magnetic field perpendicular to the polarization of
the laser, pure rotational transitions split as \( \nu = \nu_0 \pm \beta_{1g} H \), where \( \nu_0 \) 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 \( \Delta \nu = 2g_0 \beta_1 H \).

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

\[
\mu = -\frac{ch}{16\pi^2 M_p \Delta z} \frac{1}{2\beta_1 H} \left( \frac{\Delta \nu'}{B'} - \frac{\Delta \nu}{B} \right) + \frac{1}{2} Qe \Delta z,
\]

with \( \Delta z \) 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⁺
center of mass is shifted, while the distance between the atoms is kept constant. An internuclear distance $r_{\text{KrH}^+} = 1.42 \, \text{Å}$ \cite{7, 9} leads to a value for the shift in the center of mass of $\Delta z (^{84}\text{KrH}^+ \rightarrow ^{84}\text{KrD}^+) = 0.0163 \, \text{Å}$. 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 $r_c$. The experimentally determined Zeeman splitting will yield $g(r_0)$ rather than $g(r_c)$. It was therefore tried in the ArH$^+$ measurements \cite{2} to extrapolate the $g_R$ factor for both isotopes to $r_c$ and by subsequent use of Eq. (2) to determine $\mu(r_c)$. In the N$_2$H$^+$ experiment \cite{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 $^{86}\text{KrD}^+$ but the accuracy that could be achieved in determining the line positions together with the very small value of $\Delta z (^{84}\text{KrD}^+ \rightarrow ^{86}\text{KrD}^-)$ was not sufficient to yield a significant value for $\Delta z$. 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 \cite{14},

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

(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 $E_0$ are the energy of the electronically excited state $n$ and ground state 0, and $I(r)$ is the moment of inertia ($m_r^2 r^2$). From here on we will use unprimed quantities for KrH$^+$ and primed quantities for KrD$^+$.

While $g_{\text{nuc}}$ can be shown to be independent of $r$, this is not the case for $g_{\text{el}}$. If we assume that $\sum_{n \neq 0} |\langle n | L_x | 0 \rangle|^2/(E_n - E_0)$ is independent of $r$, $g_{\text{el}}$ 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 $g_{\text{el}}$ as $r^{-2}$. We then can easily obtain the dipole moment in two limiting cases:

(i) $g_R$ dominated by $g_{\text{nuc}}$. In this case $g_R = g_{\text{nuc}}$ is independent of $r$. This implies that $g_R(r_c) = g_R(r_0)$, where $g_R(r_0)$ corresponds to the measured quantities. Using this we can determine $\mu(r_c)$ according to

<table>
<thead>
<tr>
<th>Ion</th>
<th>Component</th>
<th>Frequency</th>
<th>Splitting</th>
<th>$g_R$</th>
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<tr>
<td>$^{84}\text{KrD}^+$</td>
<td>Low</td>
<td>503010.7580</td>
<td>$\rightarrow$ 21.064</td>
<td>-0.279113</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>503031.8215</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{84}\text{KrH}^+$</td>
<td>Low</td>
<td>494494.452</td>
<td>$\rightarrow$ 41.846</td>
<td>-0.554489</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>494536.298</td>
<td></td>
<td></td>
</tr>
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</table>
\( \mu(r_e) = -\frac{e^2}{16\pi^2\hbar^2m_e} \left( \frac{g'_K(r_e) - g_K(r_e)}{B'_e} - \frac{g_K(r_e)}{B_e} \right) + \frac{1}{2} Qe\Delta z. \) (4)

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

\[
g'_K(r_0) = g'_K(r'_0) \left( \frac{r'_0}{r_0} \right)^2 
\]

(5)

\[
B'(r_0) = B'(r'_0) \left( \frac{r'_0}{r_0} \right)^2.
\]

(6)

This results in

\[
\mu(r_0) = -\frac{e^2}{16\pi^2\hbar^2m_e\Delta z} \left( \frac{g'_K(r'_0)}{B'(r'_0)} - \frac{g_K(r_0)}{B(r_0)} \right) + \frac{1}{2} Qe\Delta z,
\]

(7)

where \( (g'_K(r'_0)/B'(r'_0)) = (g'_K(r_0)/B'(r_0)) \), 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 \( g'_K(r_0) = g'_K(r'_0)(r'_0/r_0)^2 = 0.2777829 \), 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 \( g_{KrD^+} = 0.985555 \) and that \( g_{KrD^+} = 0.494917 \). Before we can calculate \( g_{el} \) according to \( g_{el} = g_K - g_{nuc} \), we have to know the sign of \( g_K \).

Since \( d \) is pointing in the direction from the hydrogen atom towards the Kr atom, a negative difference of \((g'_K/B') - (g_K/B)\) implies that \( \mu \) is pointing from H towards Kr (polarity \( +\text{Kr-H}^- \)). A positive difference means that \( \mu \) 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 \( g_K \) and \( B \) values, we see that in this case \( g_K \) and \( g'_K \) (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 \( g_K \) can be extrapolated by

\[
g'_K(r_0) = g'_{nuc} + g'_{el}(r'_0) \left( \frac{r'_0}{r_0} \right)^2 
\]

(8)

if we assume that \( \sum_{n\neq0} |\langle n | L_z | 0 \rangle|^2/(E_n - E_0) \) is really independent of \( r \); \( r_0 \) and \( r'_0 \) were calculated according to the formula \( r^2 = 505379/Bm_{\text{rec}} \) MHz Å\(^2\) amu using the

### Table II

<table>
<thead>
<tr>
<th>Ion</th>
<th>( g_K )</th>
<th>( g_{nuc} )</th>
<th>( g_{el} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{KrD}^+ )</td>
<td>-0.279113</td>
<td>0.494917</td>
<td>-0.77403</td>
</tr>
<tr>
<td>( \text{KrH}^+ )</td>
<td>-0.554489</td>
<td>0.985555</td>
<td>-1.54004</td>
</tr>
</tbody>
</table>

The Nuclear and Electronic Contribution to the \( g_K \) Factor
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 \( g_{el}(r) \).

Whereas in the paper of Laughlin \textit{et al.} (2) the correction of \( \mu \) 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 \( \text{KrH}^+ \) was found to be negative. We should therefore expect to find also a negative \( g_R \) value for \( \text{ArH}^+ \), but according to Ref. (16), the sign was determined to be positive by comparing \( \text{ArH}^+ \) 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 \textit{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.

5. ACKNOWLEDGMENTS

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