

## Measurement of the electronic $g$ factor of $\text{H}_2^+$

R. Loch, R. Stengler, and G. Werth

*Institut für Physik, Universität Mainz, Postfach 3980, D-6500 Mainz 1, West Germany*

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Ion trapping and spin-dependent charge-exchange techniques were used to determine the electron  $g$  factor of  $\text{H}_2^+$  as a first step to provide a precise test of the theory of molecular  $g$  factors. Accessible to us were the vibrational states 4, 5, and 6. Averaged over these vibrational states we obtain  $g(v=4,5,6)=2.002\,283\,7(18)$  in agreement with the corresponding theoretical value of  $g=2.002\,282\,8(8)$ . As a by-product we have measured the rotational  $g$  factor to be  $g_{\text{rot}}=0.920(40)$ , compared with the calculated value of  $g_{\text{rot}}=0.9244$ .

### I. INTRODUCTION

The measurement of atomic  $g$  values provides an important source of information about the structure of atomic systems. A particular role is played by the one-electron systems such as the hydrogen atom or the  $\text{He}^+$  ion, since the electronic  $g$  factor can be calculated including radiative and relativistic corrections and thus represents a test of bound-state quantum electrodynamics. In the cases of H and  $\text{He}^+$  the result of the binding is a deviation of the electron  $g$  factor of  $-17.75$  and  $-70.9$  ppm, respectively, from the free-electron  $g$  value. Both values have been confirmed experimentally.<sup>1,2</sup>

The case of  $\text{H}_2^+$  is somewhat more complicated because of the lack of central symmetry in the potential. Hegstrom<sup>3</sup> has shown that the  $g$  factor now becomes a tensor, having components  $g_{\parallel}$  parallel and  $g_{\perp}$  perpendicular to the molecular axis. Moreover, the  $g$  value depends on the molecular vibrational and rotational state. Starting from the Breit formalism, which has been developed for many-electron atoms and which includes the electron's anomalous-magnetic-moment and nuclear-mass correction terms, and which is expected to be correct to order  $\alpha^4\mu_B B$ , where  $\alpha$  is the fine-structure constant, Hegstrom calculated the  $g$  factors for different vibrational and rotational states. While the dependence on the rotational state is less than 0.1 ppm from one state to the next, the effect of the chemical bond on  $g$  is much more pronounced for the vibrational states. The value for  $R=0$ ,  $R$  being the internuclear distance, corresponds to the singly ionized helium atom, while for  $R \rightarrow \infty$  the molecular  $g$  factor approaches the value of the hydrogen atom. In between it varies in a continuous fashion between these two limits, showing a maximum near the internuclear distance of 4.5 a.u., which corresponds to the vibrational state  $v=12$ . Figure 3 of Hegstrom's work shows the characteristic dependence for the expression

$$g_{\text{av}} = \frac{1}{3}(2g_{\perp} + g_{\parallel}), \quad (1)$$

which is accessible to observation.

### II. ZEEMAN EFFECT OF $\text{H}_2^+$

In a magnetic field of a few Tesla, as in our experiment, the different angular-momentum and spin vectors are

decoupled and we have the magnetic-field-dependent part of the Hamiltonian  $H^{\text{eff}}$ ,

$$H^{\text{eff}} = g_s\mu_B \mathbf{S} \cdot \mathbf{B} - g_k\mu_N \mathbf{K} \cdot \mathbf{B} - g_I\mu_N \mathbf{I} \cdot \mathbf{B} + H_{\text{ai}}. \quad (2)$$

$S$ ,  $K$ , and  $I$  are the electron spin, the rotational angular momentum, and the total nuclear spin.  $H_{\text{ai}}$  is the anisotropic part of the electrons  $g$  factor, which is proportional to  $(g_{\perp} - g_{\parallel})$  and about a factor of  $10^{-6}$  smaller than the other parts of the Hamiltonian. It will be neglected in the following. For the isotropic part  $g_s$  of the  $g$  factor we have  $g_s = g_{\text{av}}$ . The corresponding energy values of the  $\text{H}_2^+$  molecule in a magnetic field are

$$E = g_s\mu_B B m_s - g_k\mu_N B m_k - g_I\mu_N B m_I. \quad (3)$$

The main contribution comes from the electron magnetic moment, while the second and third parts are about a factor of 1000 smaller. The rotational  $g$  value  $g_k$  has been calculated by Hegstrom<sup>3</sup> to  $g_k=0.9244$ , which does not contain vibrational-rotational corrections. The contribution from the proton's magnetic moment is zero for parahydrogen ( $I=0$ ).

### III. EXPERIMENT

The principle of the experiment is based on the idea of spin-dependent collision techniques, outlined by Major and Dehmelt.<sup>4</sup> It has been used to determine the  $g$  factor of  $\text{He}^+$ .<sup>5</sup> Attempts have been made by the same authors to extend the method to  $\text{H}_2^+$ .<sup>6</sup> The ions are stored in an ion trap with a superimposed magnetic field. They are spin polarized by collisions with a polarized atomic beam. A spin flip, induced by a radio-frequency magnetic field, is detected by spin-dependent charge-exchange collisions with the same atomic beam. The value of the magnetic field at the position of the ions is determined by a measurement of the ion's cyclotron frequency. Figure 1 shows the experimental setup.

#### A. Storage

In our experiment we used a quadrupole Penning ion trap for ion storage as extensively described in the literature.<sup>7,8</sup> The trap electrodes, made of oxygen-free copper, are hyperboloids of revolution. This simplifies the analytical calculation of ion trajectories and oscillation frequen-

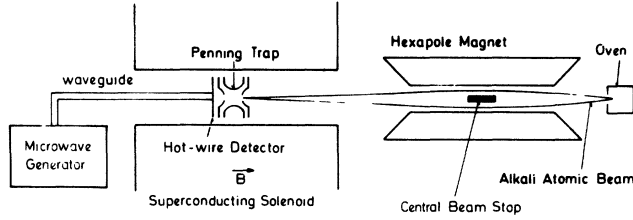


FIG. 1. Experimental setup.

cies. The magnetic field superimposed on the trap along the axis of the symmetry ( $z$  axis), was produced by a superconducting coil and could be raised to 5 T.

The trap slightly deviates from the ideal shape; holes of 4-mm diameter were drilled in the central part of the end cap electrodes to allow an atomic and an electron beam to enter the trap, and the ring electrode was divided into two symmetric parts in order to apply a radio-frequency field between them, which could excite the ions' cyclotron motion. The radius of the ring electrode  $r_0$  was 7 mm, the distance between the end caps  $2z_0 = 9$  mm and the applied voltage  $U$  was of the order of 15 V. In the ideal case the ions' motion can be described by a superposition of three oscillations: A harmonic motion along the  $z$  axis, unperturbed by the magnetic field; the cyclotron motion, slightly perturbed by the presence of the electric trapping field; and a drift of the cyclotron motion center around the trap axis (magnetron motion). The corresponding eigenfrequencies of the ion motion are

$$\begin{aligned}\omega_z &= (eU/mz_0^2)^{1/2}, \\ \omega'_c &= \omega_c/2 + (\omega_c^2/4 - \omega_z^2/2)^{1/2}, \\ \omega_m &= \omega_c/2 - (\omega_c^2/4 - \omega_z^2/2)^{1/2}, \\ \omega_c &= (e/m)B.\end{aligned}\quad (4)$$

The deviation of the trap potential from the ideal case causes small shifts of the eigenfrequencies. Brown and Gabrielse<sup>9</sup> have shown that most of those perturbations can be taken care of. By variation of the trap potential and observation of different eigenfrequencies of the ions like  $\omega'_c, \omega_m, \omega'_c + \omega_m$  we checked that the error in magnetic field determination is less than the quoted uncertainty.

The ions are created inside the trap's volume by electroionization of the background gas, which at a base pressure of  $(1-3) \times 10^{-9}$  mbar consisted mainly of  $H_2$  molecules after a bakeout of the apparatus for three days. A pulse from an electron gun of approximately 0.5 s length, 100 eV energy, and 1  $\mu$ A current was sufficient to fill the trap with about  $10^5$   $H_2^+$  ions. Elastic collisions with the background atoms limit the average storage time to about 2 s.

We detect the stored ion cloud by resonant absorption of energy from a tank circuit, whose capacity is formed by the trap's end cap electrodes, when the ion's  $z$ -oscillation frequency is swept over the tank-circuit's resonance by changing the trapping potential linearly in time. This leads to a damping of the tank circuit, which is measured by the change in amplitude of a weakly coupled rf

voltage at the eigenfrequency. After rectification and amplification we obtain an absorption signal, whose amplitude is proportional to the ion number.

### B. Polarization

The stored  $H_2^+$  ions were polarized by spin exchange collisions with polarized Na atoms. The cross section for those processes is of the order  $10^{-14}$  cm<sup>2</sup>. A sodium beam of about  $10^{12}$  atoms/s at the trap position was polarized by a hexapole magnet. Apertures at different positions along the beam and central beam stops at the hexapole axis provided a high degree of polarization of 98% as measured by laser excitation of the different Zeeman sublevels. The beam intensity was monitored by a hot-wire detector placed behind the trap.

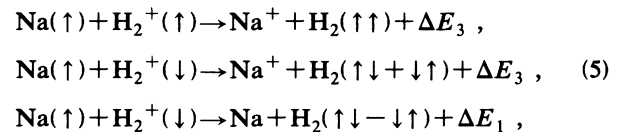
### C. Spin-flip transitions

Spin-flip transitions were induced by microwaves at 15.8 and 79.3 GHz, corresponding to the transition frequency at magnetic fields of 0.5 and 2.9 T, respectively. At 15.8 GHz the microwaves were produced by a frequency synthesizer (Systron-Donner 1618P) and guided to the hot-wire detector close to the trap, which acted as antenna. The output power of the synthesizer was 1 mW. We assume only a small fraction, which could not be measured, reached the trap volume. The frequency precision has been determined by comparison to an atomic frequency standard to be better than  $10^{-9}$ .

At 79 GHz the microwaves were produced by a backward-wave oscillator (BWO) (Siemens RWO 80) of 5 mW output power. It was frequency stabilized by a phase-locked loop, using the 5th harmonic of the microwave synthesizer as a reference. A waveguide was connected to one of the trap end cap electrodes and the microwaves entered the trap through a 4-mm hole. Frequency steps were controlled by a personal computer. Minimal step width was 1 kHz of the synthesizer and 5 kHz of the BWO.

### D. Detection of spin-flip transitions

Following a scheme outlined by Major and Dehmelt<sup>5</sup> and used by Schuessler, Fortson, and Dehmelt<sup>5</sup> to measure the hyperfine splitting of the  $^3\text{He}^+$  ground state we detect a change in the spin direction of the stored  $H_2^+$  ions by spin-dependent charge-exchange collisions. Assuming conservation of spin-angular momentum the charge-exchange processes



lead to different final states of the  $H_2$  molecule. The corresponding energy defects  $\Delta E_1$  and  $\Delta E_3$  are different and consequently we find different collision rates for the two spin directions of the  $H_2^+$  ion. The absolute value of the cross section for low kinetic energies, as in our case, de-

depends critically on the size of the energy defects.<sup>9</sup> We have determined the cross section  $Q_3$  for triplet collisions for our experimental conditions to be  $Q_3 = 1.2 \times 10^{-15} \text{ cm}^2$ .<sup>10</sup> The ratio of singlet and triplet cross sections was  $Q_1/Q_3 = 1.5 \pm 0.2$ . As shown in Ref. 10 this leads to a slightly different loss rate of  $\text{H}_2^+$  from the trap for a polarized and unpolarized Na beam. An analysis of the scattering process, however, indicates that only a few vibrational states contribute significantly to the spin-dependence of the charge-exchange process. This becomes evident from Fig. 2, where the  $\text{H}_2^+$  ground-state potential energy, reduced by the Na ionization energy, is almost resonant to the  $B^1\Sigma_u^+$  state of  $\text{H}_2$  for vibrational states  $v \geq 4$  ( $\Delta E \leq 30 \text{ meV}$ ). The energy defects along with the population (taken from Ref. 11) for vibrational states up to  $v = 6$  are listed in Table I. The population of the higher vibrational states is very small; moreover, the defect energies  $\Delta E_1$  and  $\Delta E_3$  are close to zero in both cases and consequently they would not contribute differently to the charge-exchange cross section. From this we conclude that a spin flip can be detected only for the vibrational states  $v = 4, 5, \text{ and } 6$ .

#### E. Magnetic-field measurement

The magnetic field at the position of the ions was measured by the  $\text{H}_2^+$  cyclotron resonance. It was detected by a change in signal amplitude after excitation of the ions' cyclotron orbit. The linewidth  $\delta\omega_c$  was limited by magnetic field inhomogeneities. At 0.5 T ( $\omega_c = 2\pi \times 4.3 \text{ MHz}$ ) we obtained  $\delta\omega_c/\omega_c = 7 \times 10^{-5}$  and at 2.9 T

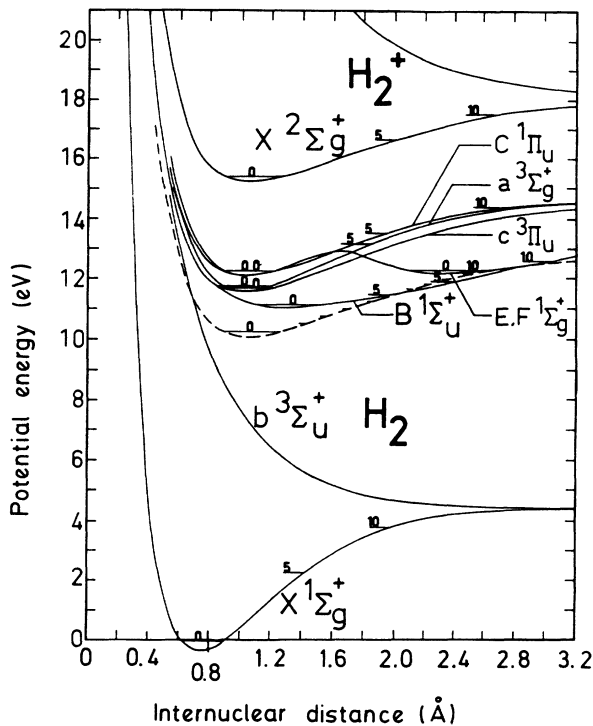


FIG. 2. Energy-level diagram of  $\text{H}_2$  and  $\text{H}_2^+$ . Dashed line:  $\text{H}_2^+$  ground-state energy reduced by the ionization potential of sodium. Vibrational states  $v > 4$  are almost resonant to the  $B^1\Sigma_u^+$  state of  $\text{H}_2$ .

TABLE I. Population of the seven lowest vibrational states of  $\text{H}_2^+$  and energy differences  $\Delta E_1$  and  $\Delta E_3$  between the  $\text{H}_2^+$  electronic ground state, reduced by the Na ionization energy, and the  $B^1\Sigma_u^+$  and  $b^3\Sigma_u^+$  states of  $\text{H}_2$ , respectively, which are the closest excited electronic states of  $\text{H}_2$ .

Vibrational state	Population	$\Delta E_1$ (meV)	$\Delta E_3$ (meV)
0	0.119	1018	1374
1	0.190	746	1032
2	0.188	492	780
3	0.152	254	573
4	0.125	32	393
5	0.075	$\sim 0$	234
6	0.052	$\sim 0$	91

( $\omega_c = 2\pi \times 21.6 \text{ MHz}$ )  $\delta\omega_c/\omega_c = 1 \times 10^{-5}$ . The relative uncertainty of the line center was  $5 \times 10^{-6}$  and  $0.4 \times 10^{-6}$ , respectively (Fig. 3). We observed a small shift in the cyclotron frequency with ion number. It is caused by the space-charge field of the ion cloud, which changes the electric-field-dependent part of the perturbed cyclotron and the magnetron motions [see Eq. (4)]. Wineland<sup>7</sup> has shown that these shifts are equal and consequently cancel in the sum  $\omega_c = \omega_c' + \omega_m'$ , if the ion cloud has the shape of a homogeneously charged ellipsoid. For other charge distributions a residual shift remains. Figure 4 shows a measurement of cyclotron frequencies for different ion numbers  $n$ . For the magnetic field strength we take the extrapolated value at  $n = 0$ .

#### IV. MEASUREMENTS AND RESULTS

Spin-flip transitions at  $\omega_L = \frac{1}{2}g(e/m)B$  were detected by measurements of the ion number remaining in the trap one second after creation by a short electron pulse (Figs. 5 and 6). As described above, the loss rate is determined by charge exchange to neutral atoms, and is different for singlet and triplet collisions with a polarized Na beam. One resonance line consists of typically 15–30 frequency steps. The signal amplitude was measured ten times at each frequency to improve the signal-to-noise ratio, each measurement lasting 1.3 s. This procedure was repeated

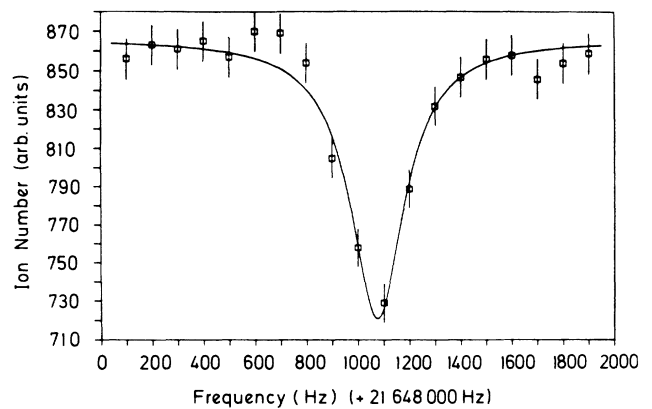


FIG. 3. Unperturbed cyclotron resonance  $\omega_c$  of  $\text{H}_2^+$  at  $B = 2.83 \text{ T}$ .

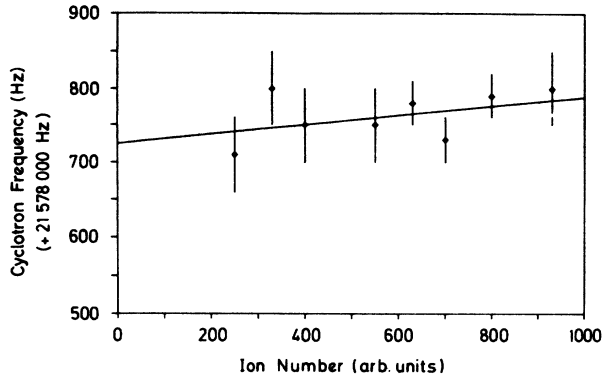


FIG. 4. Shift of the  $H_2^+$  cyclotron resonance  $\omega_c$  at different trapped ion numbers.

20 times to complete one spin-flip resonance measurement. The relative linewidth (full width at half maximum) was  $2.5 \times 10^{-5}$  at  $B=0.5$  T and  $1 \times 10^{-6}$  at  $B=2.83$  T. The resonance center was determined by a least-squares-fitted Lorentzian line shape. The statistical uncertainty was  $1 \times 10^{-6}$  and  $8 \times 10^{-8}$ , respectively. Including different measurements of the cyclotron frequency in between spin measurements, a total run lasted about 1 h.

We took five independent runs at  $B=0.56$  T and three runs at  $B=2.83$  T. From the cyclotron frequency  $\omega_c = (e/M)B$ ,  $M$  being the  $H_2^+$  mass, we determined the electronic  $g$  factor

$$g_s = 2(m/M)(\omega_L/\omega_c). \quad (6)$$

The results of the different runs are listed in Table II. The weighted average is  $g_s = 2.0022837(18)$  (0.9 ppm). The quoted errors mainly reflect the uncertainty of the cyclotron resonance frequency. At the lower magnetic field we observed a second transition caused by a simultaneous change in the rotational-orientation quantum number  $m_K$  by one (see Fig. 6). From the difference be-

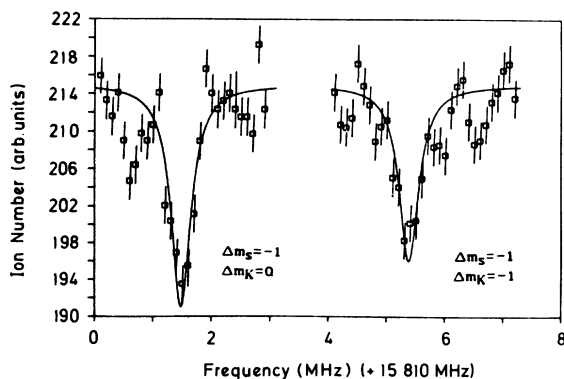


FIG. 5. Spin-flip resonance  $\Delta m_s = 1$  of  $H_2^+$  at  $B=0.56$  T. The second resonance occurs by the simultaneously changed rotational-orientation quantum number  $m_K$ .

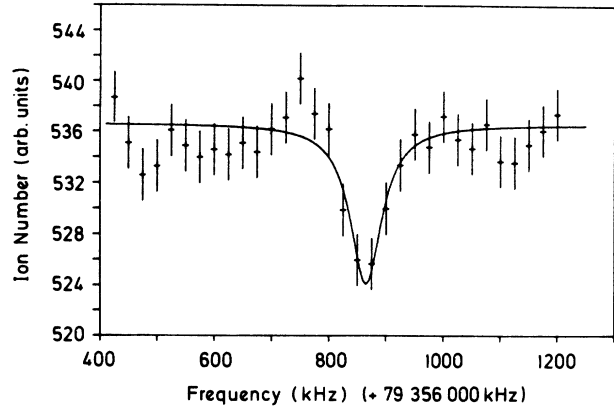


FIG. 6. Spin-flip resonance of  $H_2^+$  at  $B=2.83$  T.

tween the two frequencies we determined the rotational  $g$  value  $g_K$  [see Eq. (2)]. The result is  $g_K = 0.920(40)$ . The large error arises from the fact that we determine a small difference of two large frequencies.

## V. DISCUSSION

As discussed in Sec. III D, only the vibrational states  $v=4, 5$ , and  $6$  contribute to a spin dependence of the charge-exchange process and hence to the observed signal. To compare our experimental results with the calculation, we have to take the average  $g$  value of these states weighted with the relative population as they are listed in Table I. This gives a theoretical  $g$  value of  $g_s^{\text{th}} = 2.0022828(8)$ . Our experimental result agrees with this value within one standard deviation.

According to Hegstrom's calculation, the difference in the  $g$  value between the vibrational levels  $4, 5$ , and  $6$  is of the order of  $0.3$  ppm. A total linewidth of  $1$  ppm as obtained at  $2.83$  T obviously is not sufficiently small to resolve the different vibrational levels. The necessary improvement of about one order of magnitude is obtainable if we succeed in reducing the amplitude fluctuations of our detection signal in order to improve the signal-to-noise ratio, by employing a more homogeneous solenoid,

TABLE II. Results of independent  $g$  factor measurements.

Run no.	$B$ field (T)	$g$ value
1	0.56	2.0022850(240)
2	0.56	2.0022824(467)
3	0.56	2.0022878(364)
4	0.56	2.0023000(560)
5	0.56	2.0022852(377)
6	2.83	2.0022838(20)
7	2.83	2.0022827(53)
8	2.83	2.0022833(60)
average		2.0022837(18)

which is commercially available and working at higher field strength.

A different test of the calculation would be a measurement of the heteronuclear isotope  $\text{HD}^+$ . In this case the vibrational states relax by radiation into the ground state within a few milliseconds. In this way any ambiguity about the level would be avoided. It is an open question, however, whether or not there is a neutral atom which exhibits a sufficient spin dependence of the charge-exchange process with  $\text{HD}^+$  in order to use the same detection mechanism as in the present experiment. A possible dependence of the  $g$  value on the rotational energy levels is of the order of 0.03 ppm per rotational state.<sup>3</sup> Since only the lowest three rotational states are populated, this effect is too small to be observable at the present precision.

In summary, we have performed a measurement of the  $g$  value of the electron bound in the simplest system without central potential, and found agreement to a quantum electrodynamic calculation to the level of 0.9 ppm. This represents the first precise test of the theory of molecular  $g$  factors. As a side effect we made the first measurement of the rotational  $g$  factor. Within about 4% it agrees with a theoretical calculation.

#### ACKNOWLEDGMENTS

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