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ROTATIONAL Hfs SPECTRA OF H_2^+ MOLECULAR IONS

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Rf transitions characteristic of interaction between the electron spin and the molecular rotation have been observed in para-H_2^+. Values of the coupling coefficients (ρ-type doubling constant) are given for two vibrational states tentatively identified as $v=5$ and $v=6$. An approximate determination of the rotational magnetic moment in the rotational state $K=2$ has also been made.

Various authors[1-4] have made calculations of the hfs of H_2^+. Dalgarno *et al.* give the following Hamiltonian in zero magnetic field (coefficients in MHz):

$$H_{\rm eff} = 880\vec{I}\cdot\vec{S} + 130 I_z S_z + d\vec{S}\cdot\vec{K}$$

with d estimated to be of the order of 150 MHz. Stephen[5] has estimated d to be +46 MHz for the ground vibrational state. For para-H_2^+, $I=0$, and the Hamiltonian simplifies to

$$H_{\rm eff} = d\vec{S}\cdot\vec{K}.$$

The experimental method utilized is based upon the fact that the photodissociation rates $R(F, M_F)$ of ions in the ground ($1S\sigma$) electronic state are dependent upon F and M_F when the sample is illuminated by linearly polarized light. This is a consequence of the fact that the photodissociation reaction is an allowed electric dipole transition, with well defined selection rules.

H_2^+ ions are formed in an rf quadrupole ion trap[6,7] by electron impact from para-H_2 which is flowed through the system at a pressure of 1×10^{-8} Torr. The para-H_2 originates in a vessel containing an ortho-para-H_2 catalyst, which is refrigerated with liquid H_2. Examination of the $\Delta F=0, \Delta M_F=\pm 1$ spectra, which contain contributions from both ortho- and para-H_2^+ when the system is operated on normal H_2, indicates that the ortho-H_2 content is less than 5%.

Photodissociation is induced by an intense, linearly polarized light beam, providing an average dissociation lifetime of about 30 msec, for the ions dissociable by the light. The short-wavelength limit of the light source, about 2500 Å, limits dissociation to H_2^+ ions in the vibrations states $v \geq 4$. See Fig. 1.

Under such circumstances, the population of the trap may be described by

$$N(t) = N_0 \sum_{F, M_F} \exp\left(\frac{-R(F, M_F)t}{\tau}\right),$$

i.e., each state F, M_F dissociates with its own rate $R(F, M_F)$.

If, however, the transition between two states $F1, M_{F_1}$ and $F2, M_{F_2}$ is saturated, i.e., the populations of the states are equalized at a rate compared with the photodissociation rate, the two states involved dissociate with an average

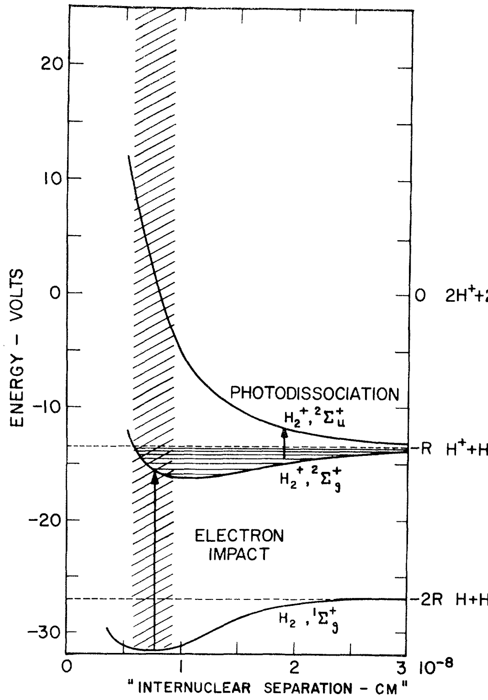

FIG. 1. Energy levels of H_2-H_2^+ system.

rate $R=\frac{1}{2}(R_1+R_2)$, with the result that, excepting the trivial case $R_1=R_2$, at any time $t>0$, there are fewer H_2^+ ions remaining than in the absence of saturation. This is all to say that the effect of such saturation is to take ions from a relatively long-lived state and transfer them to a relatively short-lived state, where they photodissociate. For a more complete discussion, see Dehmelt et al.[8]

The characteristics of the ion trap allow simultaneous trapping of the H_2^+ and the H^+ produced in the photodissociation reaction, as well as individual extraction of the species at the end of the measurement cycle. The measurement cycle (see Fig. 2) consists of a 50-msec electron burst which forms the H_2^+, a 120-msec irradiation period during which photodissociation takes place, and sequential extraction of the remaining H_2^+ and the product H^+, the whole cycle requiring 200 msec.

The ratio H^+/H_2^+ is formed by the signal processor, and stored in a multichannel digital memory as the frequency of the rf magnetic field is slowly swept. The $\Delta F=0, \Delta M_F=\pm1$ transitions, to which all vibrational states contribute in the low-field (16 mOe) region, are observed with a signal-to-noise ratio of about 4 for a single sweep.

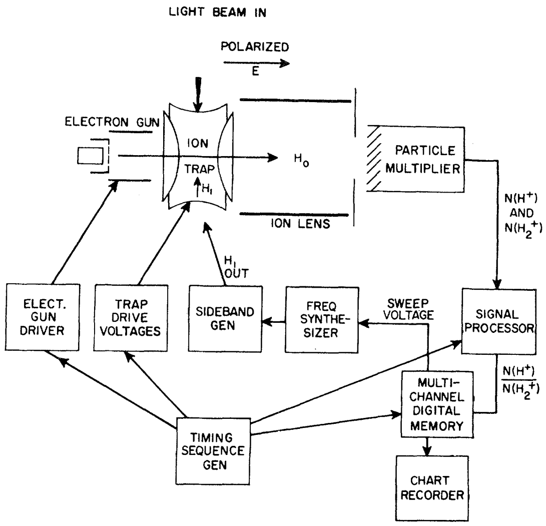

FIG. 2. Experimental block diagram.

$\Delta F=\pm1, \Delta M_F=\pm1$ transitions between the states ($K=2$)

$$F=\tfrac{5}{2},\quad M_F=\pm\tfrac{5}{2},\pm\tfrac{1}{2}$$

and

$$F=\tfrac{3}{2},\quad M_F=\pm\tfrac{3}{2}$$

have been observed by this method, for the vibrational states tentatively identified as $v=5$ and $v=6$. Intensities of these two transitions are approximately 15% of the $\Delta F=0, \Delta M_F=\pm1$ transitions.

The measurement was made in a field H_0 of approximately 16 mOe by generating a set of frequencies which simultaneously saturated the four transitions

$$\tfrac{5}{2},\tfrac{5}{2}\leftrightarrow\tfrac{3}{2},\tfrac{3}{2},$$

$$\tfrac{5}{2},\tfrac{1}{2}\leftrightarrow\tfrac{3}{2},\tfrac{3}{2},$$

$$\tfrac{5}{2},-\tfrac{1}{2}\leftrightarrow\tfrac{3}{2},-\tfrac{3}{2},$$

$$\tfrac{5}{2},-\tfrac{5}{2}\leftrightarrow\tfrac{3}{2},-\tfrac{3}{2}.$$

This was accomplished by generating sidebands at $\delta\nu=\pm2\nu_z, \pm4\nu_z$ on a carrier at ΔW_F, and then suppressing the carrier. (ν_z = frequency of observed $\Delta F=0, \Delta M_F=\pm1$ Zeeman transitions.)

The results for one transition are shown in Fig. 3. The subsidiary peaks represent points where the set of frequencies saturates one or

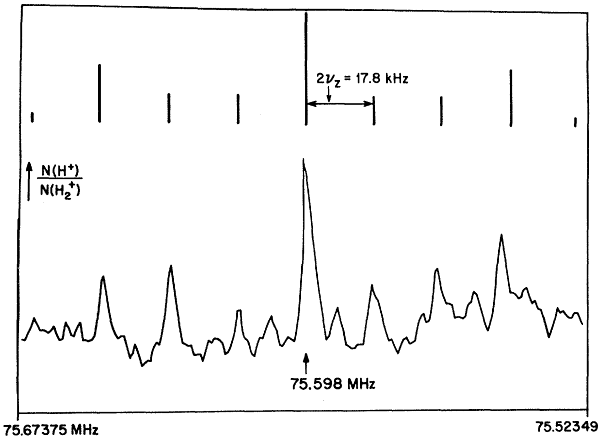

FIG. 3. $\Delta F = \pm 1$ transition, $v = 5$.

more of the above transitions. The results are

$$v = 5 \pm 1, \quad \Delta W_F = 75.598 \pm 0.002 \text{ MHz},$$

$$d = 30.239 \pm 0.001 \text{ MHz};$$

$$v = 6 \pm 1, \quad \Delta W_F = 70.231 \pm 0.002 \text{ MHz},$$

$$d = 28.092 \pm 0.001 \text{ MHz}.$$

The uncertainty in the assignment of vibrational quantum numbers can be removed by utilizing the low-wavelength limits for photodissociation from the various vibrational states, see Fig. 1.

Observation of the $\Delta F = 0, \Delta M_F = \pm 1$ transitions in the intermediate-field region (0.7 Oe) yields a rough value for the rotational moment μ_k. For the state $k = 2$, and with undetermined contributions from vibrational states $4 \leqslant v \leqslant 8$,

$$\mu_k = +1.2 \pm 0.4 \, \mu_N.$$

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ECHO BEHAVIOR IN RUBY*

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Electron spin echoes at 9.25 GHz have been observed in a dilute ruby crystal immersed in liquid helium in a magnetic field of 3.3 kG applied along the optic axis. The echoes are associated with transitions between the $m = \pm\frac{1}{2}$ levels of the ${}^4A_2$ ground state of the Cr^{3+} ion in Al_2O_3,[1] and show a marked modulation[2-4] as the separation between the two excitation pulses is increased. The electron spin echoes disappear when the magnetic field is rotated away from the optic axis by as little as three degrees just as the photon echoes disappeared in the initial photon-echo experiments in ruby.[5] The Hamiltonian describing the system of the Cr^{3+} ion and its Al neighbors, with the magnetic field applied along the optic axis of the crystal, is considered to have the form

$$\mathcal{H} = g\beta H S_z + D[S_z^2 - \tfrac{1}{3}S(S+1)] + \sum_i \{-\hbar\gamma H I_{zi} + Q^i[I_{zi}^2 - \tfrac{1}{3}I(I+1)]\} + S_z \sum_i [(A_i + B_z^i) I_{zi} + B_t^i I_{ti}],$$

where the summation is over the 13 nearest Al neighbors and the constants have been determined by the ENDOR experiment of Laurance, McIrvine, and Lambe.[6] From the above Hamiltonian we obtain an equivalent Hamiltonian which describes the Cr^{3+} ion as a simple two-level system, and we find that a density matrix calculation similar to that of Rowan, Hahn,