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High-Resolution Magnetic Hyperfine Resonance in Harmonically Bound Ground-State ^{199}Hg Ions

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The field-independent ($\Delta F = \pm 1$, $M_F' = 0 \rightarrow M_F = 0$) magnetic hyperfine transition has been observed in ground-state ^{199}Hg ions by optical pumping with a ^{202}Hg lamp. The ions were confined by a quadrupole rf electric field, imparting to them a discrete motional spectrum which leads to Doppler sidebands which can readily be resolved. The central line was observed to have a fractional linewidth not exceeding 2×10^{-10}, a degree of resolution surpassed only by the Mössbauer effect. A preliminary value for the center frequency is given as 40 507 348 050 ± 50 Hz.

The high-resolution spectroscopic study of the intrinsic interactions in an atomic system requires, in general, either the elimination of, or the ability to make a precise correction for, the effect of the state of motion of the particles and the effect of extraneous perturbations on the quantum states of interest. The manifestations of the Doppler effect in the spectra of particles interacting with radiation under different motional constraints, such as nuclei elastically bound in a crystal lattice, or particles diffusing in a gas, have in the past received considerable attention.[1] In the microwave region of the spectrum, the Dicke effect[1] has been invoked as a matter of course to minimize the first-order Doppler broadening in such diverse studies as the hfs spectrum of Cs, Rb,[2] and the H maser.[3] More recently, in the experiments on the hfs of electrodynamically stored $^3He^+$ ions, departures from the Dicke conditions enabled resolved Doppler sidebands to be detected.[4]

However, in the present work on the rf spectrum of electrodynamically suspended ions, no attempt is made to meet the Dicke criterion $ka < 1$, where k is the radiation wave number and a the amplitude of the particle motion. Indeed the discrete, well resolved, Doppler sideband structure which the oscillatory motion of the ions produces, far from being objectionable, contains useful information concerning the distribution of energy among the ions, which is required for making second-order corrections to the center line. This is evidently true wherever the inherent linewidth of a transition is much smaller than the frequencies in the motional spectrum of the particles.

The ions are produced and confined within an rf quadrupole electric field[5] whose geometry is given by $\varphi = (U_0 + V_0 \cos\Omega t) r_0^{-2}(r^2/2 - z^2)$. The equations of motion of an ion with a given e/m are of the Mathieu type, namely,

$$\ddot{x}_i + (a_i + 2q_i \cos 2\xi) x_i = 0,$$

where $\xi = \Omega t/2$; $a_r = -a_z/2 = 4eU_0/mr_0^2\Omega^2$; $q_r = q_z/2 = 2eV_0/mr_0^2\Omega^2$. For points (a_r, q_r) and (a_z, q_z) within regions of stability in the a-q plane of the Mathieu equation, the motion is oscillatory with the following discrete spectrum: $\omega_n = (2n + \beta)\Omega$, where β is a function of the a's and q's, and n is an integer. In the presence of a uniform axial magnetic field H_0, the above quantities are modified as follows: $a_r' = a_r + 4\omega_L^2/\Omega^2$; $\omega' = (2n + \beta')\Omega \pm \omega_L$, where $\omega_L = eH_0/2mc$ is the Larmor frequency. This complex oscillatory ion motion will affect the microwave absorption spectrum of ions irradiated by a plane wave in a manner contained in the autocorrelation function[1] $K(\tau) = \{\exp[i \times \vec{k}\cdot\vec{r}(t)]\ \exp[-i\vec{k}\cdot\vec{r}(t+\tau)]\}_{\text{ave}}$, where $\vec{k}$ is the wave vector and $\vec{r}(t)$ is the ion position vector at time t. Under the experimental conditions obtaining in the present work, the collision frequency of the ions with other ions and background particles is entirely negligible compared to all frequencies related to the c.m. motion of each ion. Therefore, in carrying out the statistical average, the amplitude change is imperceptibly small during the integration time for the motion. The computation is drastically simplified; however, without explicitly carrying it out using the Mathieu solution, it is evident, on the basis of the result for a simple harmonic oscillator of frequency ω, namely,

$$K(\tau) = \sum_n \int_0^{A_m} \rho(A) J_n^2(kA) \exp(-in\omega\tau)dA,$$

that one is led to a frequency spectrum consisting of a central line and sidebands at harmonic intercombination frequencies extending to $\sim k r_0 \beta\Omega$. Naturally, the detailed shape of each line for which the behavior at large τ is important requires the effect of collisions to be included.

Further, under these conditions of particle confinement, perturbation-free observation times are possible (at least to the extent that the electric fields can be disregarded) which exceed those presently attainable in spectroscopy. This was the prime motivation in the development of the *ion storage technique* as originally propounded by Dehmelt and subsequently experimentally applied in the rf studies on He^+, H_2^+, and later the free electron.[5]

In the work reported here, ultranarrow hfs ($\Delta F = 1$, $M_F' = 0 \to M_F = 0$) transitions in the ground state of $^{199}Hg^+$ were observed by optical pumping of hfs sublevel populations with the 1942-Å line from a ^{202}Hg lamp, and detecting the microwave transitions by the change in the intensity of the resonance fluorescence. This is based on the observation that, because of the isotopic shift in the ground state of the ion, there is a fortuitous matching of wavelengths between the ^{202}Hg II and ^{199}Hg II spectra. In Fig. 1(a) are depicted the relevant energy levels taken from the work of Mrozowski[6] on the spectroscopic analysis of the quadrupole $^2S_{1/2}$-$^2D_{5/2}$ line at 2815 Å and the $^2D_{5/2}$-$^2P_{3/2}$ line at 3984 Å in Hg II. A more recent study of the same quadrupole line by Loebich and Steudel[7] gives the value 1351 mK (40.5 GHz) for the $^2S_{1/2}$ hfs interval.

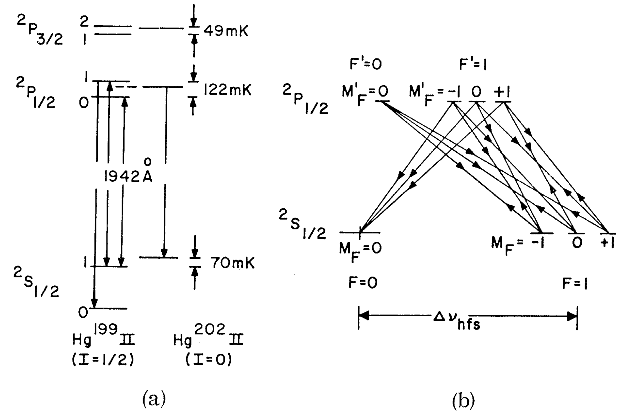

FIG. 1. (a) Hyperfine structure and isotope shifts in ^{199}Hg II and ^{202}Hg II. (b) Hyperfine optical pumping of $^{199}Hg^+$ ions using the 1942-Å line in the ^{202}Hg II spectrum.

Recognizing that the isotopic shift is negligibly small for the P states, and estimating the hfs interval for the $^2P_{1/2}$ state from the $^2P_{3/2}$ value using the Goudsmit formula, it becomes obvious that the resonance $^2S_{1/2}$-$^2P_{1/2}$ line at 1942 Å in ^{202}Hg II comes within 22 and 100 mK of connecting the $F' = 1$ and $F' = 0$ hyperfine sublevels of the $^2P_{1/2}$ state with the $F = 1$ sublevel of the ground state.[8] Because the motion of the absorbing ions causes a Doppler broadening of nearly 250 mK, there is a complete overlap of the spectral profile of the 1942-Å line from ^{202}Hg II and the $^2S_{1/2}$ $(F=1) \to {}^2P_{1/2}$ $(F'=1)$ component in ^{199}Hg II, while the $^2S_{1/2}$ $(F=0) \to {}^2P_{1/2}$ $(F'=1)$ transition is not excited, leading to the optical pumping scheme illustrated in Fig. 1(b). The time development of the population difference Δ between the $m_F = 0$ substates is easily computed to be

$$d\Delta/dt = \tfrac{2}{9}\alpha(n - \Delta) - \alpha_r \Delta,$$

where α, the quantum absorption probability per unit time, is given with sufficient accuracy by[9] $\alpha = \pi r_0 c f J_0/\Delta\omega_D$, with J_0 the quantum flux density in the 1942-Å line and r_0 the classical radius of the electron; and α_r^{-1} is the relaxation time, determined predominantly by charge exchange with background neutral Hg vapor, and spin exchange with the ionizing electron beam. The operating parameters were chosen to correspond to $\alpha_r \approx 10$ sec^{-1}. The fluorescence "signal," which will be

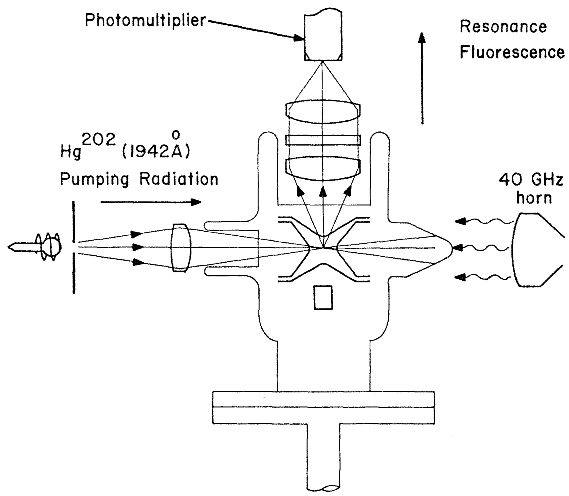

FIG. 2. Apparatus for optically observing hfs microwave transitions in $^{199}Hg^+$ ions confined in an rf quadrupole electric field.

defined as the change in the intensity of the fluorescence caused by the microwave saturation of the hfs 0-0 transition in the ground state, is given by

$$S_{\rm rf}=\tfrac{10}{17}S_0(\alpha_r\tau_p+1)^{-1}(\tfrac{4}{15}\alpha_r\tau_p+1)(\tfrac{6}{17}\alpha_r\tau_p+1)^{-1},$$

where $\tau_p^{-1}=\frac{2}{9}\alpha$, and S_0 is the intensity of fluorescence for uniform sublevel population.

The experimental arrangement is illustrated in Fig. 2. The stainless-steel quadrupole electrodes were precisely machined with the proper hyperbolic geometry with $r_0=1.13$ cm. The electron gun, using a Philips impregnated type "A" cathode, was mounted coaxially with the quadrupole. The quadrupole rf trap was operated with the following choice of parameters: $\Omega/2\pi=524$ kHz, $U_0=12$ V, $V_0=248$ $V_{\rm rms}$. To the extent that the adiabatic approximation[10] is useful, this corresponds to an effective potential well of depth 16 V with characteristic mean oscillation frequencies of 57 and 80 kHz for the radial and axial coordinates, respectively.

The ^{202}Hg II pumping source was a 1.5-cm-diam electrodeless quartz lamp excited with an input power of 20 W at 90 MHz. The brightness of these lamps at 1942 Å has been estimated at 2 $\times 10^{14}$ quanta cm^{-2} sec^{-1} sr^{-1}. The highest emission was obtained from lamps sealed off under high vacuum without any carrier gas; however, degradation in output at 1942 Å was noted in time. The optical fluorescence detection system consisted of fast ($f/1.5$) quartz optics, including a 50-mm-diam interference filter (25% transmission peaked at 1942 Å), projecting an image of the center of the quadrupole onto the 25-mm-diam cathode of a solar-blind end-on photomultiplier tube (EMR 541F). The circumstance that the resonance radiation is in the uv region, making possible the use of a solar-blind Cs-Te-cathode photomultiplier tube and an interference filter blocked in the visible, circumvents what would otherwise be amost difficult experimental problem, namely, the high background radiation from a cathode at 1000°C.

Since the hfs transition frequency was known from the optical spectroscopic data only to within perhaps 0.2%, flexibility and reserve power in the microwave system was essential. It consisted of a klystron phase locked effectively to the 1350th harmonic of a (nominal) 30-MHz signal from a 50-MHz frequency synthesizer, which could be referenced to an HP5060 cesium frequency standard. The output of the klystron, after appropriate isolation, power and frequency metering, and attenuation, feeds a high-gain horn directed at a 12-mm hole in the quadrupole cylinder, thereby irradiating the confined ions.

The experimental procedure sought firstly to establish that the contribution from the ions to the scattered light reaching the photomultiplier was large enough to be detected above the background (amounting to $\approx 3\times 10^6$ quanta sec^{-1}), and to optimize this signal using a Hg^{199} lamp. Modulation of the ion population was accomplished by alternating an ion-producing electron pulse with an ion-clearing voltage pulse applied to the quadrupole. Using standard quantum counting equipment the signal-to-noise ratio obtained was about 10:1 for effective counting times of 100 sec. Although a number of questions of a photometric nature have yet to be examined in detail, it can be said that the above results are best fitted by an ion number of 10^5.

The microwave spectrum was observed simply by sweeping the synthesizer frequency with a precise voltage ramp derived from the time base of a digital signal averager. The fluorescence detector was operated in the analog mode with a 3-Hz bandwidth. The first broad (150 kHz) field-dependent resonance was observed with about -15 dB above 1 mW of microwave power into the horn. It was recognized that the spectral purity of the 30 MHz from the synthesizer was marginally capable of permitting the observation of the very sharp 0-0 transition because of the high order of multiplication required; however, by finely adjusting the power input to the microwave

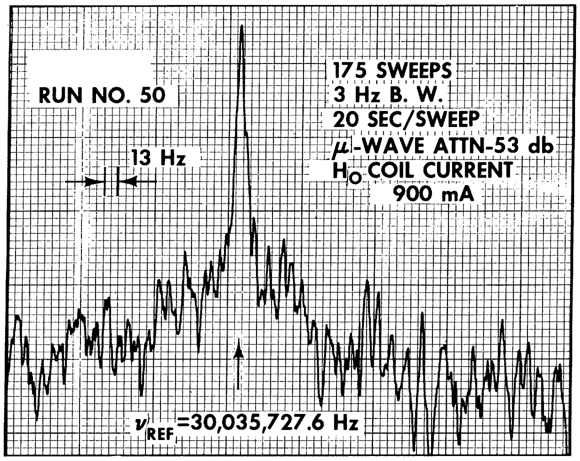

FIG. 3. Intensity of resonance fluorescence from $^{199}Hg^+$ ions as the frequency of microwave field is swept through resonance with the $\Delta F = \pm 1$, $M_F' = 0 \rightarrow M_F = 0$ transition.

horn, the 0-0 resonance signal shown in Fig. 3 was obtained, after averaging over 200 sweeps. The line center occurs at a reference frequency of 30 035 727.35 Hz, which, with a measured i.f. of 40 833 710 Hz, yields for the transition frequency, extrapolated to zero magnetic field, a value of 40 507 348 050 ± 50 Hz. The error bounds have been purposely set much wider than the actual 5-Hz statistical standard deviation obtained in the field-dependence data, since it was not our intent to enter here upon questions of absolute accuracy.

In conclusion it may be said that while the degree of spectral resolution has been amply demonstrated, a great deal remains to be done in improving the signal/noise ratio. This problem, which stems from the severely limited number of ions which can be confined, may find an effective solution in the formation and confinement of neutral heavy-ion plasmas.[11] Exploration of this possibility is currently proceeding.

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[1]See for instance K. S. Singwi and A. Sjölander, Phys. Rev. 120, 1093 (1960); S. G. Rautian and I. I. Sobelman, Usp. Fiz. Nauk 90, 209 (1966) [Sov. Phys. Usp. 9, 701 (1967)].

[2]P. L. Bender, E. C. Beaty, and A. R. Chi, Phys. Rev. Lett. 1, 311 (1958).

[3]D. Kleppner, H. M. Goldenberg, and N. F. Ramsey, Phys. Rev. 126, 603 (1962).

[4]H. A. Schuessler, E. N. Fortson, and H. G. Dehmelt, Phys. Rev. 187, 5 (1969).

[5]H. G. Dehmelt, in *Advances in Atomic and Molecular Physics,* edited by D. R. Bates (Academic, New York, 1969), Vol. 5, pp. 109–154.

[6]S. Mrozowski, Phys. Rev. 57, 207 (1940), and 58, 332 (1940).

[7]O. Loebich and A. Steudel, Z. Phys. 166, 56 (1962).

[8]We are indebted to V. Kaufman of the National Bureau of Standards, Gaithersburg, Maryland, for helping to verify this point by obtaining high-resolution spectrograms of our lamps on a 10-m vacuum spectrograph.

[9]A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge Univ. Press, Cambridge, England, 1961), p. 96.

[10]F. G. Major and H. G. Dehmelt, Phys. Rev. 170, 91 (1968).

[11]F. G. Major and J. P. Schermann, Bull. Amer. Phys. Soc. 16, 838 (1971).