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Spin-Exchange Shifts in the Hydrogen Maser*

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Spin-exchange pulling of the $\Delta m_F=0$ ground-state hyperfine transition in atomic hydrogen is investigated for the case of self-excited oscillation on this transition in the hydrogen maser. Frequency shifts due to mistuning the maser cavity are found to compensate spin-exchange shifts so that both can be effectively eliminated. The result bears importantly on the use of the hydrogen maser as a spectroscopic tool and frequency standard and suggests a method for determining the spin-exchange shift parameter.

I. INTRODUCTION

FREQUENCY pulling of transitions between ground-state atomic-hydrogen hyperfine levels due to spin-exchange collisions has been treated by several authors.[1–4] In particular, Bender has used the exchange operator introduced by Wittke and Dicke[5,6] to calculate the time rate of change of the hydrogen spin-space density matrix due to exchange and has applied the result to the $F=1$, $m_F=0\rightarrow F=0$, $m_F=0$ transition in the atomic-hydrogen maser.[7–10] He finds that when power broadening and relaxation effects other than exchange are unimportant, a semiclassical estimate of the exchange shift-to-linewidth parameter predicts a maximum shift of roughly 1% of the full transition linewidth. If spin exchange contributed the only significant variation of the oscillation frequency with linewidth, such a large shift would be easily observable, and the precision of such an observation would very likely set the limit of accuracy of the hydrogen maser as a spectroscopic tool and as a primary frequency standard.

There is an additional pulling of the oscillation frequency due to mistuning of the maser microwave cavity.[9,10] Cavity pulling depends on linewidth in such a way that if the cavity is tuned so that no change of oscillation frequency is observed as the linewidth is varied, spin-exchange and cavity pulling effects cancel to a high order of accuracy.[3] Although this result has played an important role in experimental determinations of the hyperfine separation in atomic hydrogen,[11] the Stark shift of the hydrogen hyperfine separation,[12] the hyperfine separation in atomic tritium,[13] and the hydrogen spin-exchange shift parameter itself,[3,4] details of the analysis have not been published previously.

In Sec. II, the results of Bender are extended to include cavity pulling and power broadening at power levels set by the oscillation conditions. In Sec. III the analysis is extended to cases when relaxation mechanisms other than hydrogen-hydrogen spin exchange are significant. An experiment in which the hydrogen-hydrogen shift-to-linewidth parameter can be more precisely determined against a background of such extraneous relaxations is described in Sec. IV.

II. RELAXATION BY HYDROGEN-HYDROGEN EXCHANGE ONLY

A. Spin-Exchange Shift

Bender's result for the power radiated by atoms undergoing hydrogen exchange collisions while stimulated to make $F=1$, $m_F=0\rightarrow F=0$, $m_F=0$ ground-state hyperfine transitions by a rf magnetic field having frequency ω is [Ref. 1, Eq. (25)]

$$P=\tfrac{1}{4}I_{\mathrm{tot}}\hbar\omega\, x^2/[1+T_2^2(\omega-\omega')^2](T_1T_2)^{-1}+x^2\,, \tag{1}$$

where

$$T_2^{-1}=T_b^{-1}+\tfrac{1}{2}T_{\mathrm{H}}^{-1}\,, \tag{2}$$

$$T_1^{-1}=T_b^{-1}+T_{\mathrm{H}}^{-1}\,. \tag{3}$$

I_{tot} is the total hydrogen atom input beam intensity, and x is $\mu_0/\hbar$ times the amplitude of the rf magnetic

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[3] S. B. Crampton, Ph.D. thesis, Harvard University, 1964 (unpublished).

[4] S. B. Crampton and D. Kleppner, Bull. Am. Phys. Soc. **9**, 451 (1964). The last sentence of this reference should read: "Spin-exchange shifts of the order of 1% of a 40-cps change in linewidth of the $\Delta m_F=-1$ oscillation frequency and 0.5% of a 1-cps change in linewidth of the $\Delta m_F=0$ oscillation frequency are in agreement⋯."

[5] J. P. Wittke and R. H. Dicke, Phys. Rev. **103**, 620 (1956).

[6] J. P. Wittke, Ph.D. thesis, Princeton University, 1955 (unpublished).

[7] H. M. Goldenberg, D. Kleppner, and N. F. Ramsey, Phys. Rev. Letters **5**, 361 (1960).

[8] D. Kleppner, H. M. Goldenberg, and N. F. Ramsey, Appl. Opt. **1**, 55 (1962).

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

[10] D. Kleppner, H. C. Berg, S. B. Crampton, N. F. Ramsey, R. F. C. Vessot, H. E. Peters, and J. Vanier, Phys. Rev. **138**, A972 (1965).

[11] S. B. Crampton, D. Kleppner, and N. F. Ramsey, Phys. Rev. Letters **11**, 338 (1963).

[12] E. N. Fortson, D. Kleppner, and N. F. Ramsey, Phys. Rev. Letters **13**, 22 (1964).

[13] B. S. Mathur, S. B. Crampton, D. Kleppner, and N. F. Ramsey, this issue, Phys. Rev. **158**, 14 (1967).

field averaged over the maser storage bottle.[14] T_b is the average length of time spent by an atom in the maser storage bottle, and T_H^{-1} is the exchange collision rate

$$T_H^{-1}=n(\mathrm{H})\bar{v}\sigma, \tag{4}$$

where $n(\mathrm{H})$ is the density of atoms in the storage bottle, $\bar{v}$ is their mean relative speed, and σ is the spin-exchange cross section.[15,16]

The frequency ω' is shifted from the density-independent[17] resonance frequency ω_0 by [Ref. 1, Eq. (24)]

$$\omega'-\omega_0=-\tfrac{1}{4}(\rho_{22}-\rho_{44})\lambda/\sigma T_H, \tag{5}$$

where λ is the spin-exchange shift parameter[18] and $\rho_{22}-\rho_{44}$ is the average difference in population between the $m_F=0$ hyperfine levels, given by [Ref. 1, Eq. (22)]

$$\rho_{22}-\rho_{44}=\frac{\frac{1}{2}[1+(\omega-\omega')^2T_2^2](T_2T_b)^{-1}}{[1+(\omega-\omega')^2T_2^2](T_1T_2)^{-1}+x^2}. \tag{6}$$

When the maser oscillates on this transition, the amplitude of the rf magnetic field in the cavity (measured in units of $\sec^{-1}$ by the parameter x) is such that the power dissipated in the cavity walls and output coupling loop is equal to the radiated power. The power dissipated has been calculated by Kleppner, Goldenberg, and Ramsey[9] to be

$$P=\omega V_c x^2\hbar^2/8\pi\eta Q\mu_0^2, \tag{7}$$

where Q is the cavity quality factor, V_c is the cavity volume, and η is the filling factor relating the z component of the cavity rf magnetic field averaged over the storage bottle to the square of the total rf magnetic field averaged over the cavity. Equating Eqs. (1) and (4) gives

$$[1+(\omega-\omega')^2T_2^2](T_1T_2)^{-1}+x^2=2\pi I_{\mathrm{tot}}\,\eta Q\mu_0^2/\hbar V_c. \tag{8}$$

The density of atoms in the bottle (of volume V_b) is $n(\mathrm{H})=(I_{\mathrm{tot}}T_b)/V_b$, so that in terms of linewidth parameters

$$I_{\mathrm{tot}}=V_b/\bar{v}\sigma T_bT_H. \tag{9}$$

With (9), Eq. (8) becomes

$$[1+(\omega-\omega')^2T_2^2](T_1T_2)^{-1}+x^2=2/mT_bT_H, \tag{10}$$

where the maser quality factor $m=\pi\mu_0^2\eta QV_b/\bar{v}\sigma\hbar V_c$ determines the range of input beam intensities over which the maser will oscillate.[19] For example, in the simple case when exchange is the only appreciable relaxation mechanism, m must be equal to or less than 0.686 in order that the maser oscillate at all. At $m=0.686$, the maser oscillates only at the beam intensity for which $T_b=\sqrt{2}T_H$ and only at frequencies well within the resonance linewidth.[20]

With the oscillation conditions (10) substituted into the denominator of the level population difference (6) the spin-exchange frequency shift becomes

$$\omega'-\omega_0=-(m\lambda/16\sigma)[1+(\omega-\omega')^2T_2^2]T_2^{-1}. \tag{11}$$

In the limit that the maser quality factor has the maximum value consistent with oscillation, Eq. (11) predicts a ratio of spin-exchange shift to full resonance linewidth equal to the amount found for this ratio by neglecting power broadening,[1] since in this limit for m the rate x is small compared to the relaxation rates and $(\omega-\omega')T_2\ll 1$. The significant difference is that when the maser is oscillating the shift depends on the sum $T_2^{-1}=T_b^{-1}+\frac{1}{2}T_H^{-1}$ rather than on only that part of T_2^{-1} due directly to exchange collisions. Equation (11) holds only over the range of spin-exchange collision rates for which the oscillation conditions (10) are satisfied. For example, the oscillation conditions are satisfied for zero spin-exchange collision rate only in the limit $m=0$, when the shift (11) is also zero.

B. Cavity Pulling

The amplitude and phase of a single microwave cavity mode interacting with radiating atoms are conveniently described by a complex cavity quality factor Q_m, using a result given by Slater[21] for a cavity containing a microwave current. Q_m has been found by Kleppner, Goldenberg, and Ramsey[9] for the case when the atoms are described by a spin-space density matrix in which $T_1=T_2$. In this case the calculation is the same as their Sec. II C, except that the starting point is the solution for the density matrix given by Bender.[1] The result is

$$Q_m^{-1}=Q^{-1}+i\left(\frac{\omega}{\omega_c}-\frac{\omega_c}{\omega}\right)+\frac{2i[1+(\omega-\omega')T_2](T_HT_b)^{-1}}{mQ[1+(\omega-\omega')^2T_2^2](T_1T_2)^{-1}+x^2}, \tag{12}$$

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[14] The notation has been changed to agree with the notation of Ref. 10, which includes a detailed description of the conditions for oscillation on the $\Delta m_F=0$ transition in the hydrogen maser.

[15] A. F. Hildebrandt, F. B. Booth, and C. A. Barth, J. Chem. Phys. 31, 273 (1959).

[16] R. M. Mazo, J. Chem. Phys. 34, 169 (1961).

[17] The density-independent resonance frequency ω_0 differs from the zero magnetic-field hydrogen hyperfine separation frequency by the magnetic field dependence of the energy levels, the wall shift, and the second-order Doppler effect, as discussed in Ref. 11.

[18] In the limit of classical collision trajectories $n(\mathrm{H})\bar{v}\sigma$ and $n(\mathrm{H})\bar{v}\lambda$ reduce to the exchange linewidth parameter $\frac{1}{2}U$ and the exchange shift parameter V, respectively, of Ref. 1. σ and λ are defined more generally in terms of the phase shifts for hydrogen-hydrogen scattering in Eqs. (21) and (22).

[19] The factor m is closely related to the quality factor q of Ref. 10. For exchange relaxation only, q reduces to $\frac{1}{4}m$; in the general case the conditions for oscillation are more complicated, as described in Ref. 10, Sec. II.

[20] The range of beam intensities over which the maser oscillates is determined by the product $m[1+(\omega-\omega')^2T_2^2]$. The factor $[1+(\omega-\omega')^2T_2^2]$ can be made larger than unity by mistuning the cavity so that it pulls the oscillation frequency outside the resonance linewidth.

[21] J. C. Slater, Rev. Mod. Phys. 18, 441 (1946).

where ω_c is the cavity resonance frequency in the absence of the microwave current.

The condition for self-excited oscillation is that the real and imaginary parts of Q_m^{-1} be zero. The real part of Eq. (12) for $Q_m^{-1}=0$ reproduces Eq. (10), while the imaginary part provides the relation

$$(\omega-\omega')T_2=(\omega_c/\omega-\omega/\omega_c)Q. \tag{13}$$

Equations (11) and (13) combine to give

$$(\omega-\omega_0)T_2=Q\left(\frac{\omega_c}{\omega}-\frac{\omega}{\omega_c}\right)-\frac{m\lambda}{16\sigma}\left[1+Q^2\left(\frac{\omega_c}{\omega}-\frac{\omega}{\omega_c}\right)^2\right]. \tag{14}$$

The oscillation power level is given by Eq. (7) as proportional to x^2, which with Eq. (13) becomes

$$x^2=\frac{2}{mT_bT_{\mathrm{H}}}-(T_1T_2)^{-1}\left[1+Q^2\left(\frac{\omega_c}{\omega}-\frac{\omega}{\omega_c}\right)^2\right]. \tag{15}$$

Equation (15) describes the oscillation power level observed over the range of quality factors and relaxation rates for which it is positive, and Eq. (14) provides the oscillation frequency observed when that condition is satisfied.

C. Discussion

There is one value of ω_c for which the right-hand side of Eq. (14) is zero while at the same time Eq. (15) is satisfied for positive x^2. At this position of cavity tuning the maser oscillates at its unshifted resonance frequency ω_0 at all values of T_2 over which it oscillates at all.[22] The behavior of the oscillation frequency for values of ω_c near this value is most easily illustrated by expanding Eq. (14) in the small parameters $(\omega-\omega_0)/\omega_0$ and $(\omega_c-\omega_0)/\omega_0$. The leading term is

$$(\omega-\omega_0)T_2=\frac{(2Q/\omega_0)(\omega_c-\omega_0)-m\lambda/16\sigma-(m\lambda/16\sigma+1/4Q)[(2Q/\omega_0)(\omega_c-\omega_0)]^2}{1+(2Q/\omega_0T_2)[1-2(m\lambda/16\sigma)(2Q/\omega_0)(\omega_c-\omega_0)]} \tag{16}$$

plus terms of order 10^{-8} or smaller compared to this term under normal operating conditions. A preliminary measurement[3,4] of λ/σ using alternate oscillations on two ground-state hyperfine transitions is in qualitative agreement with Bender's semiclassical estimate[1] of $\lambda/\sigma=+0.4$, and m must be 0.686 or less, so that $m\lambda/16\sigma$ is of order 10^{-2}. Q is normally of order 10^4. $2Q/\omega_0T_2$ is equal to the ratio of atomic resonance width to cavity width and is normally of order 10^{-3} or less. Because of the small sizes of the parameters $m\lambda/16\sigma$, $2Q/\omega_0T_2$, and $1/4Q$, the variation of $\omega-\omega_0$ for values of ω_c near the tuned position is described primarily by

$$(\omega-\omega_0)=[(2Q/\omega_0)(\omega_c-\omega_0)-m\lambda/16\sigma]T_2^{-1} \tag{17}$$

plus terms nonlinear in T_2^{-1} which are of order 10^{-3} or smaller compared to these. The approximately linear variation of ω with $\omega_cT_2^{-1}$ for values of ω_c near the tuned position makes it possible to correct ω to ω_0 without knowing either the spin-exchange shift parameter or T_2. An appropriate tuning procedure has been described in a previous paper.[23]

III. EFFECTS OF OTHER RELAXATIONS

In practice there are several mechanisms other than hydrogen-hydrogen exchange which relax atoms radiating in a hydrogen maser. The most significant of these are due to collisions between the atoms and the interior surface of the storage bottle. Surface relaxations which are independent of the density of hydrogen atoms and are therefore easily distinguished from hydrogen-hydrogen exchange include chemical reactions and magnetic relaxation by gradients due to nuclear spins in the wall material. In addition, Berg has observed spin-exchange relaxation of radiating hydrogen atoms by unpaired electron-spin sites on the storage surface.[24] This background spin exchange is particularly difficult to distinguish from hydrogen-hydrogen exchange when, as has been observed, the rate of background spin exchange is proportional to the hydrogen atom density. Fortunately, the correlation times associated with these surface interactions are short enough compared to the relaxation times that the time evolution of the spin-space density matrix $\rho(\mathrm{H})$ effectively separates into a sum of time-independent terms, each of which is linear in one of the relaxation rates. Steady-state solution for the elements of $\rho(\mathrm{H})$ involves simultaneous solution of a set of nonlinear algebraic equations whose terms are not known separately in general. Nevertheless, it is possible to obtain a useful solution for the density-dependent frequency shift of the $F=1$, $m_F=0\rightarrow F=0$, $m_F=0$ transition based on the following assumptions:

(1) The time rate of change of the hydrogen spin-space density matrix due to hydrogen-hydrogen exchange collisions is described by the result of Balling, Hanson, and Pipkin (Table X of Ref. 2). Their result reduces in the limit of classical trajectories to the result found by Bender, but it provides a more general description in terms of the scattering phase shifts for binary collisions and includes the effects of hydrogen atom identity.

(2) The only frequency shifts which vary with the hydrogen atom density are those due to hydrogen-

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[22] The other three roots are negative or so far from the hydrogen resonance as to preclude oscillation even at infinite cavity Q.

[23] Reference 10, Sec. X.

[24] H. C. Berg, Phys. Rev. **137**, A1621 (1965).

hydrogen exchange and cavity pulling. The frequency of the $F=1$, $m_F=0\rightarrow F=0$, $m_F=0$ transition in hydrogen has been shown both theoretically and experimentally to be unshifted by collisions with deuterium atoms,[3] and the result has been extended theoretically to collisions with oxygen molecules (spin 1) and N^{14} atoms (spin $\frac{3}{2}$) as well as to other spin-$\frac{1}{2}$ atoms. This assumption is therefore reasonable if the only relaxations whose rates are proportional to the hydrogen atom density are spin-exchange effects.

With these assumptions the hydrogen density matrix rate equations can be solved formally, as follows[3]:

$$\rho_{42}(\mathrm{H})=\frac{[1+(\omega-\omega')\tau_2]\frac{1}{2}x(\tau_p)^{-1}e^{i\omega t}}{[1+(\omega-\omega')^2\tau_2{}^2](\tau_1\tau_2)^{-1}+x^2}, \qquad (18)$$

$$\rho_{22}(\mathrm{H})-\rho_{44}(\mathrm{H})=\frac{[1+(\omega-\omega')^2\tau_2{}^2](\tau_2\tau_p)^{-1}}{[1+(\omega-\omega')^2\tau_2{}^2](\tau_1\tau_2)^{-1}+x^2}, \qquad (19)$$

where $(\tau_2)^{-1}$ is the sum of all the relaxation rates in the rate equation for $\rho_{42}(\mathrm{H})$, $\tau_1{}^{-1}$ is the sum of all terms in the rate equations which deplete the population difference $\rho_{22}(\mathrm{H})-\rho_{44}(\mathrm{H})$ in direct proportion to $\rho_{22}-\rho_{44}$, and $\tau_p{}^{-1}$ is the sum of all terms in the rate of change of the population difference not directly proportional to $\rho_{22}-\rho_{44}$. Equations (18) and (19) represent only formal solutions in that the rates $\tau_1{}^{-1}$, $\tau_2{}^{-1}$, and $\tau_p{}^{-1}$ depend in general on unknown relaxation rates and on the elements of $\rho(\mathrm{H})$. The diagonal effects have been arbitrarily separated into terms in $\tau_1{}^{-1}$ and $\tau_p{}^{-1}$ for convenience.

ω' is again related to the density-independent resonance frequency ω_0 by

$$\omega'-\omega_0=-\tfrac{1}{4}(\rho_{22}-\rho_{44})\lambda/\sigma T_{\mathrm{H}}, \qquad (20)$$

where the cross section and shift parameter are[2]

$$\sigma=\bar{v}^{-1}\langle(\pi\hbar/\mu k)\sum_l(2l+1)\sin^2(\delta_l{}^1-\delta_l{}^3)\rangle_k, \qquad (21)$$

$$\lambda=\bar{v}^{-1}\langle(\pi\hbar/\mu k)\sum_{l=0}^{\infty}[1+(-1)^l](2l+1) \times\sin 2(\delta_l{}^1-\delta_l{}^3)\rangle_k. \qquad (22)$$

Here $\bar{v}$ is again the mean relative speed of the hydrogen atoms, and $T_{\mathrm{H}}{}^{-1}=n(\mathrm{H})\bar{v}\sigma$. The $\delta_l{}^1$ and $\delta_l{}^3$ are the singlet and triplet scattering phase shifts, respectively, for binary collisions having orbital angular momentum l and relative linear momentum $\hbar k$. The indicated average is over relative collision momenta $\hbar k$.

The derivation of frequency-pulling effects and oscillation power levels from Eqs. (18)–(20) follows the argument of Sec. II. The results are

$$(\omega-\omega_0)\tau_2=Q\left(\frac{\omega_c}{\omega}-\frac{\omega}{\omega_c}\right)-\frac{m\lambda}{16\sigma}\left[1+Q^2\left(\frac{\omega_c}{\omega}-\frac{\omega}{\omega_c}\right)^2\right], \qquad (14')$$

$$x^2=\frac{4}{m\tau_p T_{\mathrm{H}}}-(\tau_1\tau_2)^{-1}\left[1+Q^2\left(\frac{\omega_c}{\omega}-\frac{\omega}{\omega_c}\right)^2\right], \qquad (15')$$

$$(\omega-\omega_0)=[(2Q/\omega_0)(\omega_c-\omega_0)-m\lambda/16\sigma]\tau_2{}^{-1}. \qquad (17')$$

Again there is a value of cavity resonance frequency ω_c at which the oscillation frequency is unshifted from ω_0 over the full range of the linewidth parameter $(\tau_2)^{-1}$ for which x^2 is positive. The extraneous relaxations, both density-dependent and density-independent, do not affect the density-dependent pulling effects except to contribute to the linewidth and to generally weaken the oscillation power level, as discussed in a previous paper.[10] The arguments given at the end of Sec. II about the correction of the observed oscillation frequency to ω_0 are therefore generally valid, subject only to the condition that the density-dependent relaxations be spin-exchange effects.

IV. MEASUREMENT OF THE SHIFT PARAMETER

The arguments of Secs. II and III suggest that the parameter

$$\frac{m\lambda}{16\sigma}=\frac{\hbar^2V_c}{16\mu_0{}^2\eta QV_b}\left\langle\frac{1}{\mu k}\sum_{l=0}^{\infty}[1+(-1)^l](2l+1) \times\sin 2(\delta_l{}^1-\delta_l{}^3)\right\rangle_k \qquad (23)$$

can be measured by measuring the cavity-resonance frequency for which there is no variation of oscillation frequency ω with τ_2. At that value of ω_c the relation between cavity frequency and shift parameter is

$$(2Q/\omega_0)(\omega_c-\omega_0)=m\lambda/16\sigma \qquad (24)$$

plus terms of order $(m\lambda/16\sigma)^2\approx 10^{-4}$ compared to this one. Measurement of the shift paramerer to 10% by this technique would require determination of the cavity-resonance frequency to about 0.1% of the cavity-resonance width. Changes of ω_c by this amount can be detected by modulation techniques, but the terms nonlinear in ω_c are too small to permit detection of $m\lambda/16\sigma$ by measuring changes of ω_c, even with the use of external power gain. An alternative is to detect a change in pulling for a change in $m\lambda/16\sigma$ at the same setting of ω_c. The filling factor η can be varied by allowing the radiating atoms to visit a second storage bottle outside the microwave cavity. Control of flow between the two bottles by a trap door would permit variation of η without disturbing ω_c.

The spin-exchange cross section σ is largely dominated by the large scattering phase shifts at low impact parameter. The model[5,25] which assumes that $\sin^2(\delta_l{}^1-\delta_l{}^3)$ contributes $\frac{1}{2}$ for all impact parameters inside a strong collision radius and zero for all larger impact parameters is in agreement with the present experimental result[14,15]

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[25] A. E. Glassgold and S. A. Lebedeff, Ann. Phys. (N. Y.) 28, 181 (1964).

within the experimental error of about 15%. On the same model the large phase shifts at low impact parameters do not contribute to λ, which should therefore be a more sensitive test of the hydrogen-hydrogen interaction at long range. An experiment to measure λ by varying η is under way in this laboratory.

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Dissociative Ionization of H_2 and D_2[†]

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Energy distributions of H^+ (D^+) from dissociative ionization of H_2 (D_2) are reported. Evidence of the $2p\sigma_u$ state's being the major source of energetic ions is cited. Calculated and measured energy distributions do not agree well. Possible explanations are suggested.

I. INTRODUCTION

In an earlier communication[1] we reported measurements of the energy distribution of protons from the dissociative ionization of H_2 by electron impact which were in much better agreement with the predictions of the Franck-Condon principle than previous experiments had indicated. There remained, however, enough discrepancy between the experiment and theory that it seemed worthwhile to improve upon both the experiment and the calculation to try to see wherein the discrepancies could lie. This paper reports improved calculations and measurements of the proton energy distribution, and also presents data and calculations for D^+ from dissociative ionization of D_2. Although the H_2 and D_2 data are consistent with each other, they disagree with results of the improved calculations. Evidence indicates that most of the atomic ions come from the dissociative $2p\sigma_u$ state of H_2^+, the only state considered in calculating the predicted energy distribution.

II. CALCULATIONS

In our previous[1] evaluation of the predicted energy distribution of protons we invoked a form of the Franck-Condon principle and showed the energy distribution to be proportional to the quantity

$$\Theta_{v\epsilon}{}^2 = \left| \int \chi_v(R)\chi_\kappa(R)dR \right|^2 . \tag{1}$$

Here $\chi_v(R)$ and $\chi_\kappa(R)$ are the radial wave functions for the bound H_2 and repulsive H_2^+ states respectively and R is the internuclear separation. The vibration quantum number v for bound states and wave number κ for continuum states are used as subscripts.

We approximated $\chi_\kappa(R)$ by a normalized δ function. This function was defined at the classical turning point R_1 for particles of reduced mass μ with relative energy $\epsilon = \kappa^2/\mu$ in the potential of the repulsive $2p\sigma_u$ state of H_2^+. In this approximation,

$$\Theta_{v\epsilon}{}^2 = S^2 |\chi_v(R_1(\epsilon))|^2 , \tag{2}$$

where R_1 is the classical turning point and S is a normalization constant.

It was speculated in that work[1] that remaining discrepancies between predicted and measured energy distributions may in part be explained by the inadequacy of the δ function approximation to $\chi_\kappa(R)$. Hence it seemed desirable to attempt a more accurate evaluation of $\chi_\kappa(R)$ and thus of $\Theta_{v\epsilon}{}^2$.

In the approximation of the Born-Oppenheimer separability of variables, the resulting radial equation in atomic units is

$$\left[\frac{d^2}{dR^2} + \kappa^2 - \mu V(R) - \frac{K(K+1)}{R^2} \right] \chi_\kappa(R) = 0 , \tag{3}$$

where $V(R)$ is the effective internuclear potential including the electronic eigenenergy for the repulsive state, and where K is the rotational quantum number. This equation was solved numerically for several values of κ, using $V(R)$ for the $2p\sigma_u$ state of H_2^+ given by Bates, Ledsham, and Stewart.[2] The wave function

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[1] G. H. Dunn and L. J. Kieffer, Phys. Rev. **132**, 2109 (1963).

[2] D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. London **A246**, 215 (1953).