Plasma-Broadened Cesium Lines*†

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Profiles of isolated plasma-broadened lines have been calculated and measured for the fundamental series ($5D$-nF) of cesium. The calculations used the static theory for the ion interactions and the classical path, nonadiabatic impact approximation for the electron interactions. The necessary matrix elements have been obtained from wave functions specially determined for this purpose. The calculations were made for plasma ion densities in the range from 3×10^{13} to 1×10^{16} cm^{-3} and temperatures from 2000° to 10 000°K. A scanning monochromator was used to measure profiles of lines emitted from a hot-cathode low-voltage discharge. Plasma densities and electron temperatures were determined from continuum intensity measurements. Line intensities were also measured. Observations were made at ion densities from 3.2×10^{13} to 1.6×10^{15} cm^{-3} with temperatures between 2300° and 6000°K. Experimental and theoretical widths are presented and compared. The ratio of measured to calculated width averaged over the data points is 0.99 ± 0.18. The widths are nearly proportional to ion density and are insensitive to temperature. Predicted values of line shift are also given.

I. INTRODUCTION

INTEREST in line broadening has renewed in the last few years because of the large amount of recent plasma work. The line shapes obtained by spectroscopic examination of the emission of a plasma can yield inforformation about the plasma density. In this paper the plasma-broadened shapes of fundamental series lines of cesium are investigated, both theoretically and experimentally, for plasma conditions ranging from 10^{13} to 10^{16} cm^{-3} in ion density and from 2000° to 10 000°K in temperature.

Similar investigations have been done for hydrogen[1] and for helium.[2] The extension to cesium[3,4] is desirable because of the frequent use of cesium plasmas in laboratory experiments. In addition to the fundamental series lines reported here, widths of the sharp and diffuse series have been measured.[5] The fundamental series lines are more useful for the conditions considered here because their widths (one to twenty angstroms) are easily measured and are insensitive to temperature, and reabsorption is less serious.

The theory of plasma line broadening has been brought to a fine state of completeness by the recent work of Baranger and of Kolb and Griem.[6] Their use of the nonadiabatic impact approximation for electrons and the usual quasi-static theory for ions has given excellent results for the line shapes of hydrogen and helium.[7] This same procecure is used here with similar success. A classical treatment is used for the motion of the electrons, while the electric field distribution of Mozer and Baranger[8] is used for the ions. The validity of these approximations has been well established by the work on hydrogen and helium. For the present work, only isolated lines are considered in the calculations.

The profiles of 14 fundamental series lines ($5D$-nF) have been measured in a steady-state plasma. Owing to the unresolved spin-orbit splitting of the F levels in cesium and also because the broadening is almost entirely caused by perturbations of the upper state, lines originating in the same F level are not considered separately. Thus, the final states $5D_{3/2}$ and $5D_{5/2}$ are both denoted simply as $5D$.[9]

In Sec. II the measurements and apparatus are discussed. Sec. III covers the broadening calculations, and Sec. IV presents and compares the theoretical and experimental results. The accuracy of the results is discussed in Sec. V.

II. EXPERIMENT

The lines were emitted from the inter-electrode region of a plane-parallel hot-cathode cesium diode. Cathode temperatures ranged between 2150° and 2500°K. Two different cathode materials, tantalum and UC:ZrC ($\varphi\sim3.35$ eV), were used; each produced about half of the data reported here. For both cases the anode was made of copper and was cooled to about 600°K by circulating silicone oil. The electrodes were 16 mm in

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[1] H. R. Griem, A. C. Kolb, and K. Y. Shen, Phys. Rev. **116**, 4 (1959); B. Mozer. Ph.D. thesis, Carnegie Institute of Technology, 1960 (unpublished).

[2] H. R. Griem, M. Baranger, A. C. Kolb, and G. Oertel, Phys. Rev. **125**, 177 (1962).

[3] L. Agnew and P. M. Stone, Bull. Am. Phys. Soc. **7**, 275 (1962); P. M. Stone, Los Alamos Scientific Laboratory Report LA-2625, 1961 (unpublished).

[4] H. R. Griem (to be published). Professor Griem has generously furnished us with a preprint of his paper, in which he calculates line profiles for argon and cesium.

[5] Lewis Agnew and C. Summers, in The Proceedings of the Symposium on Thermionic Power Conversion, Colorado Springs, May 14–17, 1962 (to be published).

[6] M. Baranger, Phys. Rev. **111**, 481 (1958); **111**, 494 (1958); **112**, 855 (1958); A. C. Kolb and H. R. Griem, *ibid.* **111**, 514 (1958).

[7] H. F. Berg, A. W. Ali, R. Lincke, and H. R. Griem, Phys. Rev. **125**, 199 (1962). See also references 1 and 2.

[8] B. Mozer and M. Baranger, Phys. Rev. **118**, 626 (1960).

[9] Each transition denoted by $5D$-nF represents two lines with essentially identical shapes and different intensities. The lines actually measured are, in angstroms: 8018 and 8081 ($5D$-$5F$), 7228 and 7280 ($5D$-$6F$), 6826 and 6870 ($5D$-$7F$), 6629 ($5D$-$8F$), 6432 and 6473 ($5D$-$9F$), 6326 and 6366 ($5D$-$10F$), 6250 and 6289 ($5D$-$11F$), and 6232 ($5D$-$12F$).

diam and were spaced either 1.4 mm apart (UC:ZrC emitter) or 6 mm apart (tantalum emitter). The cesium vapor pressure was varied between 1.6 and 2.2 mm Hg and was controlled by maintaining equilibrium with cesium liquid at appropriate condensation temperatures (560° to 580°K). Observations were made at currents ranging from zero to 30 A/cm^2, the latter flowing at an applied voltage of 4 V dc. All line profiles were measured with a scanning monochromator equipped with a photomultiplier attachment. A tungsten strip lamp was used as a standard for the photomultiplier calibration. The diode and the associated apparatus are described more fully elsewhere.[10]

The measurements, all made in a plane parallel to the electrodes, showed homogeneous emission from the interior region of the discharge with insignificant emission from edge regions except for resonance lines. The temperature and ion density of the plasma were determined by absolute intensity measurements of both lines and continuum. Theoretical oscillator strengths due to Stone[11] were used in line measurements and Mohler's[12] experimental results for free-bound transitions into the first excited state ($6P$) were used for the continuum data.

For lines, the intensity (I_L) of a transition $i \rightarrow f$ at thermal equilibrium at a temperature T is given by

$$I_L \propto f(i,f)N(0)\exp(-E_i/kT), \tag{1}$$

where $f(i,f)$ is the oscillator strength for the transition, $N(0)$ is the population of the ground state, and E_i is the energy of the initial state. E_i and all the factors omitted from Eq. (1) are well known.

For the continuum intensity (I_c), evaluating at the $6P$ limit,

$$I_c \propto N_e^2\sigma(0)T_e^{-3/2}, \tag{2}$$

where N_e is the ion density (which is equal to the electron density in a low-temperature neutral plasma), $\sigma(v)$ is the cross section for recombination into the $6P$ state [evaluated in Eq. (2) for electrons of zero velocity], and T_e is the electron temperature where a Maxwell velocity distribution is understood. Mohler's[12] experimental value of $\sigma(v)$ allows a determination of T_e from the shape of the continuum. The determination of T_e and N_e from the continuum requires only a Maxwell velocity distribution for the electrons, a condition that always exists in the relatively dense plasma considered here. A more detailed discussion of (1) and (2) is found in reference 10.

III. CALCULATIONS

The plasma broadening of emission lines is treated by investigating the alteration in the wave functions of the atom due to the perturbing effects of the plasma ions and electrons. Transitions are assumed to be a change of state of a single electron, and hence only one-electron wave functions are required. For cesium, with one valence electron, this is certainly valid. The perturbers are assumed to be sufficiently far away that the interaction with the atom can be approximated by the first term in a multipole expansion, i.e.,

$$V_i = -\mathbf{d}\cdot\boldsymbol{\mathcal{E}}_i, \tag{3}$$

where $\boldsymbol{\mathcal{E}}_i$ is the electric field of the ith perturber at the nucleus of the radiating atom and $\mathbf{d}$ is the dipole moment of the atom.

The difference in the equilibrium velocities of ions and electrons result in different approximations for the treatment of their effects. The slow-moving ions can often be treated by the quasi-static theory. They are assumed to be motionless during the time necessary for the ion perturbations to alter significantly the unperturbed atomic Hamiltonian. Their contribution is to shift the levels by Stark effect.

The electrons can usually be treated in the impact limit. This requires that close collisions be distinct (separated in time) and take place in a time short compared to the time necessary for electron effects to alter significantly the unperturbed Hamiltonian. The weak collisions are treated by perturbation theory. The effects can be reduced to a calculation of the scattering matrix for a single collision. Then an average over the possible electron configurations is required and this is done by assuming their motion to be classical. They are taken to have a Maxwell distribution of velocities, to be randomly distributed in space, and to travel in straight paths. It has been shown[13] that the equations so obtained are equivalent to those from a quantum mechanical treatment of the electron motion.

If w_i and w_e are the half-widths[14] (in units of $2\pi\times$frequency) of the lines when only ions or only electrons are present, the validity criteria for the two limits are

$$\tau_e \ll 1/w_e, \quad \text{impact limit}$$
$$\tau_i \gg 1/w_i, \quad \text{quasi-static limit}$$

where τ_i and τ_e are average collision times for ions and electrons, respectively. A suitable estimate of the collision time is the average interparticle distance divided by the average velocity. Calculated widths are used in the criteria but a rough estimate of validity can be obtained by using the experimentally observed linewidth in the above inequalities.

The equations are greatly simplified when only isolated lines are considered. This means that neighboring energy levels do not overlap. When l degeneracy of neighboring levels is present the lines are not isolated, e.g., hydrogen lines are never isolated. High-level transitions in most atoms are not isolated, while low-

[10] L. Agnew, E. Salmi, and C. Summers (to be published).
[11] P. M. Stone, preceding paper [Phys. Rev. **127**, 1151 (1962)].
[12] F. L. Mohler, J. Research Natl. Bur. Standards **17**, 849 (1937); Revs. Modern Phys. **1**, 216 (1929). See also reference 10.
[13] M. Baranger, Phys. Rev. **112**, 855 (1958).
[14] All widths are measured at half-maximum intensity. The half-width is one-half the full width, even for asymmetrical lines.

level transitions usually are isolated, becoming non-isolated at high plasma densities (large perturbing effects). The broadening calculations are simplified for isolated lines because fewer levels are involved. Moreover, broadening of the lower level can usually be neglected compared to broadening of the upper level.

With the above approximations and restrictions, the line shape for a transition from an initial level E_i to a final level E_f is, as shown by Griem, Baranger, Kolb, and Oertel[15] (GBKO),

$$I(\omega)=\frac{w}{\pi}\int_0^\infty \frac{W(\mathcal{E})d\mathcal{E}}{w^2+(\omega-\omega_0-d-\alpha_i\mathcal{E}^2)^2}, \tag{4}$$

where $\omega_0=\hbar^{-1}(E_i-E_f)$, $W(\mathcal{E})d\mathcal{E}$ is the ion electric field distribution (probability of the ions producing an electric field in the interval $d\mathcal{E}$ about $\mathcal{E}$), α_i is the second-order Stark coefficient (no first-order term for isolated lines), and w and d are the half-width and shift due to electron effects. An average value of the Stark coefficient has been used for each of the m-degenerate states of the level. This is given by

$$\alpha_i=\frac{e^2}{3\hbar^2}\sum_k(\omega_i-\omega_k)^{-1}|\mathbf{r}_{ik}|^2, \tag{5}$$

where $\omega_i=\hbar^{-1}E_i$ and $\mathbf{r}_{ik}$ is the unperturbed matrix element between levels i and k of the position operator $\mathbf{r}$. The sum is over all states of the system (each k implies a sum over the m-degenerate states of the k level) but only those with $l_k=l_i\pm1$ give nonzero contributions and only those for which $(\omega_i-\omega_k)$ is small give non-negligible contributions. Thus, it is sufficient to limit the sum to a few nearby states. The electron width and shift are

$$w=N_e\int f(v)dv \times\left[\pi v\rho_{\min}{}^2+\frac{4\pi}{3}\left(\frac{e^4}{\hbar^2v}\right)\sum_k|\mathbf{r}_{ik}|^2a(z_{ik\min})\right],$$
$$d=N_e\frac{4\pi}{3}\left(\frac{e^4}{\hbar^2}\right) \times\int f(v)dv\frac{1}{v}\sum_k|\mathbf{r}_{ik}|^2\,\mathrm{Sn}(z_{ik}{}^{\min})b(\tfrac{3}{4}z_{ik}{}^{\min}), \tag{6}$$

with

$$z_{ik}{}^{\min}\equiv\omega_{ik}\rho_{\min}/v.$$

The $f(v)dv$ is the velocity distribution, Sn denotes "sign of" ($\pm$), and $a(x)$ and $b(x)$ are functions given by GBKO. The $\rho_{\min}$ is a minimum impact distance below which perturbation theory is invalid. It is assumed that a collision with such an impact distance completely interrupts the radiation process (scattering matrix=0). This is the most drastic assumption and is permissible since these strong collisions contribute only about 20% of the broadening. The value of $\rho_{\min}$ recommended by GBKO is that given by

$$\frac{2}{3}\left(\frac{e^2}{hv\rho_{\min}}\right)^2\left\{\left[\sum_k|\mathbf{r}_{ik}|^2A(z_{ik}{}^{\min})\right]^2+\left[\sum_k|\mathbf{r}_{ik}|^2B(z_{ik}{}^{\min})\right]^2\right\}^{1/2}=(3/4)^{3/2}. \tag{7}$$

The $A(x)$ and $B(x)$ are another set of functions given by GBKO. The functions $A(x)$, $B(x)$, $a(x)$, and $b(x)$ represent complicated integrals, the first two accounting for the proper time average and the last two accounting for the integral over all possible impact distances. The choice of $\rho_{\min}$ given by Eq. (7) makes w and d agree with adiabatic theory when $z_{ik}{}^{\min}\gg1$ (low temperature or large ω_{ik}) and agree with perturbation theory when $z_{ik}{}^{\min}\approx0$ (high temperature or $\omega_{ik}\approx0$).

IV. RESULTS AND COMPARISONS

The line profile measurements cover a range in ion density from 3.2×10^{13} to 1.6×10^{15} cm^{-3} and a range in temperature from 2300° to 6000°K. For all cases the measured values of T and T_e are in agreement within their precision of measure; and measured values of N_e agree with equilibrium values calculated from the Saha equation.

The calculations have been performed for a similar set of conditions. Wave functions calculated for cesium[11] are used to obtain the matrix elements of Eqs. (5), (6), and (7). Actually the line profiles do not depend in any sensitive way on the details of the wave functions. For states considered here, i.e., F levels, the use of hydrogen wave functions would give almost identical results.[16] The sum in Eq. (5) was limited to the six nearest perturbing levels and the quantity $(\omega_i-\omega_k)$ was obtained from cesium energy levels tabulated by Moore.[17] Since we are concerned with F levels, the most important perturbations are due to the nearby G levels, two of which ($5G$ and $6G$) are tabulated. The energies of the four necessary additional G levels were estimated by assuming a constant quantum defect for these levels. The actual splittings used were 39 cm^{-1} for the $5F$–$5G$ splitting, 17 cm^{-1} for $6F$–$6G$, 15 cm^{-1} for $7F$–$7G$, 11 cm^{-1} for $8F$–$8G$, 8 cm^{-1} for $9F$–$9G$, and 6 cm^{-1} for $10F$–$10G$.

Figures 1(a) and (b) present the measured and calculated widths vs ion density for fundamental series lines. The solid lines are calculated results and the symbols represent measured values. The ratio of experimental to theoretical width (evaluated at the measured density) has an average and standard deviation of 0.99 ± 0.18

[15] H. R. Griem *et al.*, reference 2.

[16] Bates and Damgaard matrix elements (Coulomb wave functions) are used with good results in reference 4.

[17] C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1958).

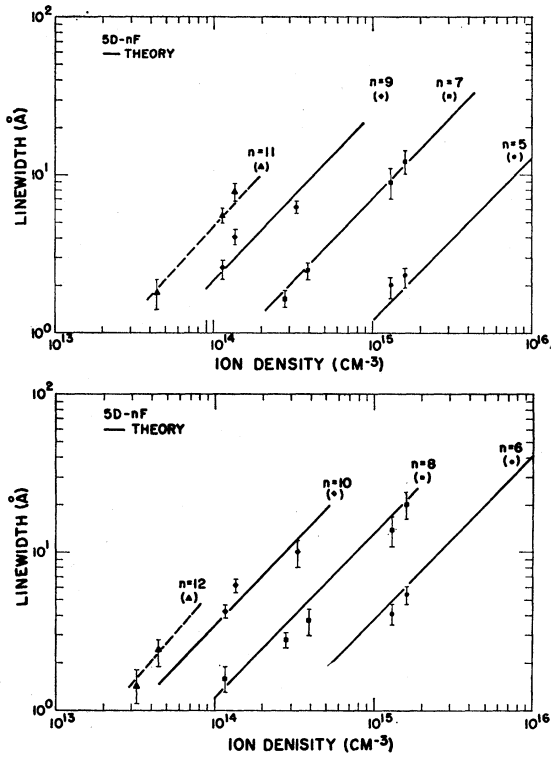

FIG. 1. Widths of cesium lines. The solid lines give the theoretical relationship between ion density and full width (at half maximum intensity) for fundamental series lines ($5D$-nF) of cesium. Measured widths are given by the data points. Dashed lines are experimental, not theoretical. Calculations are at 3000°K, while measurements are between 2300°K and 6000°K. Temperature effects are not important (see text). The data are presented in two graphs to avoid a cluttered difficult-to-read single graph; (a) gives odd n and (b) even n. The ratio of experimental to theoretical width (evaluated at the measured ion density) is 0.99 ± 0.18 when averaged over all data points.

for all data points. The results are presented in two graphs for greater legibility; there is no difference in method, selection, or presentation of the data. It is not our intent to obscure the fact that two data points (at 1.4×10^{14} cm^{-3}) fall nearest calculated widths for the next higher line. All calculated results were done for a temperature of 3000°K. While some widths were measured at temperatures as high as 6000°K (data above 10^{15} cm^{-3}), most of the data are for the range 2300° to 3000°K. The dependence of widths on temperature is discussed below.

Figure 2 shows the calculated shift of peak as a function of plasma density. The shifts are all toward longer wavelengths. Systematic measurements of shift were not attempted, but semi-quantitative results are available for the $5D$–$6F$ (7280 Å) line. The observed shift was ≈1 Å to the red at $N_e=1.6\times10^{15}$ cm^{-3} and $T=6000$°K. The calculated shift under these conditions is 1.85 Å. This agreement is acceptable considering the accuracies involved.

The linewidths given in Fig. 1 apply to any temperature in the range 2000° to 5000°K. The variation in width at a given ion density is calculated to be only a few percent over this temperature range and is much less than experimental and theoretical inaccuracies. In fact, raising the temperature to 10 000°K changes the width (usually a decrease) by less than 10%. In the experiment no clear demonstration of temperature independence can be claimed, but the data are consistent with such independence. The shifts have been calculated for $T_e=3000$°K. The shifts decrease with increasing temperature at constant ion density. For example, the $5D$–$10F$ line shift at 5.0×10^{14} cm^{-3} decreases 30% when the temperature reaches 10 000°K. Such temperature behavior can be inferred from the equations. In (6), the two terms for the electron width roughly balance when the temperature is varied, while the electron shift behaves approximately like the average of v^{-1}. The ions are assumed motionless in the theory and so their only temperature effect is through a variation of the electric field distribution. The shape of the field distribution does not change significantly, but the average electric field does change. Thus, the ion contribution to width is insensitive to temperature while the ion shift is increased with increasing temperature. The width due to both ions and electrons is then only slightly temperature dependent while the shift decreases slower than $\langle 1/v\rangle$.

The calculated widths and shifts are nearly proportional to density as is typical for isolated lines. The electron effects are strictly proportional to N_e [see Eq. (6)], while the ion effects contribute to the total broadening in a way that is insensitive to the ion density. The asymmetry of the lines is due to ion effects.

The extent of the solid lines in Figs. 1 and 2 indicates the region where the approximations involved are valid. At the lower end of the lines the static theory begins to become invalid, but this is not yet serious because the core of the line is dominated by electron effects. Extending the lines upward is risky because the lines quickly become nonisolated and the calculations are inaccurate.

Figures 3 and 4 compare experimental and theoretical profiles for the $5D$–$6F$ line at 1.6×10^{15} cm^{-3} and the $5D$–$10F$ line at 1.14×10^{14} cm^{-3}. The $5D$–$6F$ line (Fig. 3)

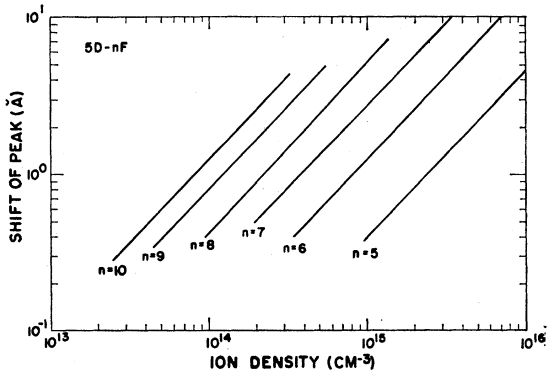

FIG. 2. Calculated values of shift of peak vs ion density for fundamental series lines ($5D$-nF) of cesium at 3000°K.

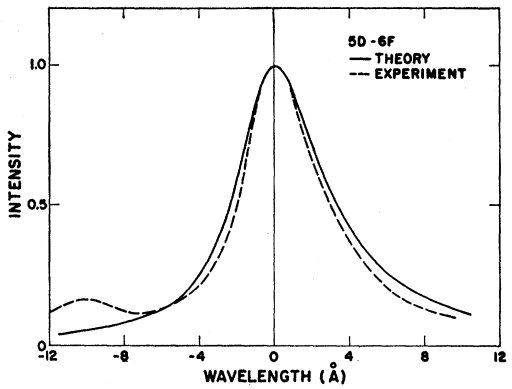

FIG. 3. Experimental and theoretical profiles of the $5D$-$6F$ line at 1.6×10^{15} ions/cm^3. The wavelength scale is centered at the peaks of the lines and the peaks are normalized to unity. The normally forbidden $5D$-$6G$ transition is clearly seen in the experiment.

clearly shows the normally forbidden component[18] $5D$–$6G$ on the lower wavelength side. The difference between the calculated and observed curves on the lower wavelength side of the $5D$–$10F$ profile (Fig. 4) is plotted in the upper left corner. It indicates qualitatively that the difference may be partly due to the forbidden transition $5D$–$10G$, expected to peak at about 3 Å on the lower wavelength side. This component seems to contribute about 10% to the width, but the line still may be considered isolated. At higher densities there may be some question as to the isolation of this line, but the calculational methods used here are still expected to be correct within the over all accuracies. Similar statements apply to the $5D$–$9F$ transitions.

In Figs. 3 and 4, the wavelength scale is centered at the peaks of the lines and the peaks have been normalized to unity. Usually the normalization procedure would be to match the areas under the experimental and theoretical profiles. This would be misleading here because the experimental curves include the forbidden transitions which raise the wings. The differences in fit near the half-maximum point as a result of a change in normalization are small and would not alter any conclusions.

V. ACCURACY

The experimental linewidths are of little value without accurate knowledge of the plasma conditions, especially ion density. As mentioned earlier, the ion density is obtained from continuum measurements supported by line intensity measurements and equilibrium considerations. Both line measurements and continuum measurements have limited accuracies: intensities are measured to about 10%, vapor pressures are known to about 10%, the cross section for recombination is probably not better than 20%, and oscillator strengths have not been verified beyond about 40%. In spite of these inaccuracies, fairly accurate knowledge of N_e and T is still possible. For example, when $E_i \gg kT$, T can be known to 10% from line intensity measurements if $N(0)fI_L^{-1}$ is known to a factor of 2. Also, N_e can be known with twice the precision that $I_c T_e^{3/2}\sigma^{-1}(0)$ is known. Upon evaluating these sources of error we conclude that N_e is known with an accuracy of about 20% for the data presented here.

Linewidth measurements are limited in accuracy by several factors; among them are poor resolution, reproducibility, overlapping of lines, and reabsorption. In dealing with monochromator resolution, we have made corrections for the instrumental width (0.3 Å in second order) for some of the narrower lines, but in all cases such corrections were of minor importance. A test of run-to-run reproducibility showed a standard deviation of 8% in measured widths. This deviation is presumably due to minor fluctuations and undetected differences in ion density. Very broad lines ($\approx$10 Å) are difficult to measure accurately because they merge into the continuum or the wings of nearby lines, making a determination of the half-maximum point difficult. The lower series members are partially reabsorbed (about 15% for $5D$–$5F$ lines and 4% for $5D$–$6F$ lines) and a correction has been made for this effect. All of these factors were considered in assigning the error bars in Fig. 1.

It is difficult to determine the over-all accuracy of the calculations, but an estimate can be made. It is reasonable to assume no more than 10% error in shifts and widths due to inaccuracies in the wave functions and 10% from the use of impact theory for electrons. The quasi-static theory for ions introduces less error because the ions give a smaller contribution to the width; a value of 5% is reasonable here. Temperature effects give errors of less than 3%. Neglecting the broadening of the lower level adds 1%. The classical treatment of the electron motion is very good, causing errors of less than 1%. Some error is introduced in the determination

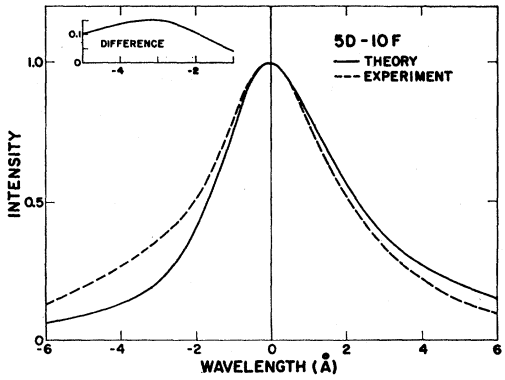

FIG. 4. Experimental and theoretical profiles of the $5D$-$10F$ line at 1.14×10^{14} ions/cm^3. The wavelength scale is centered at the peaks of the lines and the peaks are normalized to unity. The difference of the curves (experiment minus theory) is shown in the upper left corner. It suggests that the normally forbidden $5D$-$10G$ transition is partly responsible for the discrepancy. This transition should peak at about 3 Å below the main peak.

[18] This transition appears because of state mixing due to plasma perturbations.

of the energy difference between interacting levels, i.e., the energy denominator in the perturbation theory treatment of the quadratic Stark effect [see Eq. (5)]. The largest terms are due to interactions between F levels and G levels. As mentioned earlier, two of the pertinent G levels are known (with uncertain accuracy) and four others must be estimated. Effects due to error in the energy denominator are not simply related to linewidth, but any reasonable estimate of the energies of the G levels leads to differences of 20% at very most. The over-all inaccuracy is then probably about 20%.

In light of the errors involved, the experimental and theoretical agreement is quite good. The average ratio of experimental to theoretical width of 0.99 ± 0.18 is well within either the experimental or theoretical error.

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Effect of Electrostatic Interactions on the Nuclear Magnetic Resonance Dipolar Hyperfine Structure with Strong Correlation-Time Narrowing*

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The effect of electric fields on the nuclear magnetic resonance dipolar hyperfine spectrum of a liquid with correlation-time narrowing is examined. A first-order molecular quadrupole effect and a second-order molecular electric dipole effect (Stark effect) of observable magnitude are predicted. The results are discussed with reference to the proton magnetic resonance in water.

INTRODUCTION

IN an experiment for measuring the radio-frequency resonance of nuclear magnetic moments in a liquid, one observes that which is known as a strong narrowing in the limit of short correlation time.[1] The effect is simply that the time domain, the radio-frequency field, sees only the average frequency of the nuclear magnetic resonance (NMR) signal as perturbed by molecular motion. Any orientation-dependent hyperfine structure such as a dipolar hyperfine structure will thus be averaged in time by molecular motion when the correlation time of that motion τ_c is short enough so that the hyperfine frequency $\gamma\hbar\Delta H$ is much less than τ_c^{-1}. The time-averaging process is difficult to imagine, but we may conveniently predict the effect of this time averaging by carrying out an ensemble average at an instant of time. Such an average will properly weight angular positions of the molecule to give a result equivalent to a time average. This point is a bit subtle, but it should be noted that it is necessary to make a distinction between a time average, which the NMR calculations require, and an ensemble average, which allows the ready evaluation of this time average but is not otherwise physically significant.

The import of this paper is to point out that two simple molecular parameters, the molecular electric dipole moment and the molecular electric quadrupole moment, are of fundamental importance in determining the orientation statistical weights and, since they are known for many molecules, the observation of the correlation-time-narrowed NMR spectra of nuclei having dipolar hyperfine structure in these molecules will allow a partial description of the electric fields that the molecule "sees," or conversely, if the fields are known, the possibility of the determination of the first two electric moments of the molecule.

Take, for example, the water molecule H_2O^{16}. The nuclear spin of O^{16} being zero, and the spins of H^1 being 1/2, we have only the interaction terms, because of the proton moment that arises from the spin-spin isotropic and anisotropic coupling, the spin-molecular rotation coupling and the spin-Zeeman term measuring the nuclear coupling with the applied external magnetic field.

In a series of beautiful experiments the splittings in the NMR spectra of the proton and the deuteron in

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† Fulbright Lecturer, Institut Fourier, University of Grenoble (Isère), France, 1961–1962.

[1] A. Abragam, *Nuclear Magnetism* (Oxford University Press, New York, 1961), Chap. X.