Self-Broadening of Optical Double Resonance Lines in Cadmium*

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Collision broadening studies have been made of optical double resonance lines in cadmium. The results indicate that the collision frequency *is* velocity dependent, contrary to the usual theory of resonance self-broadening. This result supports the suggestion that the broadening results from interactions involving a number of intermediate states rather than only the initial and final states of the optical transition, because of the small oscillator strength ($f=0.002$) for transitions between the $(5s)^2\,{}^1S_0$ ground state and the excited state in question $(5s5p)\,{}^3P_1$. The cross section in this case has a $1/\bar{v}_{12}{}^{2/5}$ velocity dependence, so the collision frequency varies as $\bar{v}_{12}{}^{3/5}$. Measurements show that under this assumption the self-broadening cross section for cadmium is

$$\sigma_{\text{coll}}=(1.9\pm0.3)\times10^{-12}\ \text{cm}^2/\bar{v}_{12}{}^{2/5},$$

where $\bar{v}_{12}$ is the average relative velocity in cm/sec. In the course of this work, the lifetime of the $(5s,5p)\,{}^3P_1$ state was redetermined and found to be $(2.39\pm0.04)\times10^{-6}$ sec.

I. INTRODUCTION

SINCE the original work by Bitter and Brossel[1] on mercury, the method of optical double resonance has been used extensively in determining atomic g values and in studying the properties of the nucleus as they may be deduced from the interaction of nuclear matter with atomic electrons. In particular, the group II metals, mercury, zinc, and cadmium, and similar substances which have a diamagnetic $(ns)^2\ {}^1S_0$ ground state and a metastable $(ns,\ np)\ {}^3P_1$ excited state have furnished an abundance of stable and radioactive isotopes for investigation. This work is a report on a study of the collision self-broadening of the double resonance lines in the lowest $^3P_1$ state of cadmium. The results are compared with the theory of this broadening.[2] During the course of this work, the radiative lifetime of this state was also determined and the coherence narrowing[3] of the double resonance line was observed.

The shape and width of the double resonance line were studied with a standard double resonance spectrometer[4] over a range of temperatures corresponding to a density range of 10^{11} atoms/cc to 10^{15} atoms/cc. A typical half-width plot is shown in Fig. 1 ($n\bar{v}_{12}{}^{3/5}/\pi$ is the abscissa rather than n, for reasons discussed later). The slight dip in the curve is a result of coherence narrowing of the line, and the eventual rapid increase with density represents the effect of collision self-broadening.

The self-broadening of the double resonance line due to cadmium-cadmium collisions offers a particularly interesting case in which one can hope to make approximations sufficiently realistic to calculate the collision cross section[2] in a region where the usual adiabatic approximations are clearly invalid because of the close spacing of the energy levels (30 to 150 Mc/sec). Assuming a distance of closest approach, b, of about 10^{-7} cm and an average velocity of 4×10^4 cm/sec, the relevant frequencies present in a Fourier analysis of the collision will be of order $v/b=4\times10^{+11}$ cps, which is a factor of 10^4 larger than the typical Zeeman frequencies. In such a situation an application of the correlation function approach of Anderson[5] has been

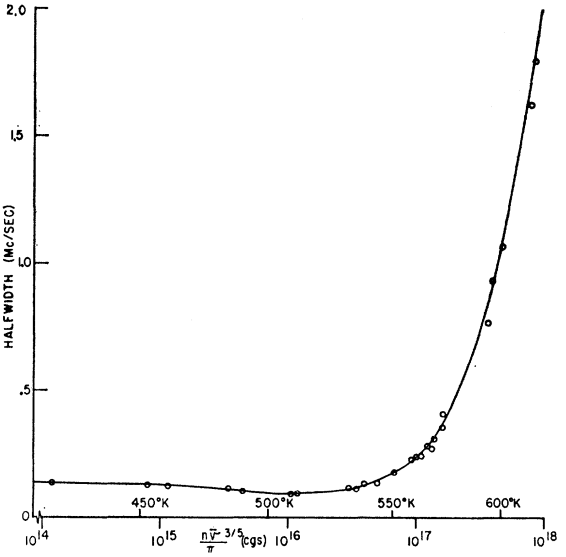

FIG. 1. The half-width of the $I=0$ resonance in natural cadmium as a function of $n\bar{v}_{12}{}^{3/5}/\pi$ over the entire range of operation.

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[1] J. Brossel and F. Bitter, Phys. Rev. **86**, 308 (1952).

[2] F. W. Byron, Jr., and H. M. Foley, following paper, Phys. Rev. **134**, A625 (1964), hereinafter referred to as BF.

[3] J. P. Barrat, J. Phys. Radium **20**, 541, 633, 657 (1959), hereinafter referred to as Barrat.

[4] M. N. McDermott and R. Novick, Phys. Rev. **131**, 707 (1963) hereinafter referred to as MN.

[5] P. W. Anderson, Phys. Rev. **76**, 647 (1949), hereinafter referred to as Anderson.

found possible,[2] and observations of double resonance lines in cadmium offer a test of the resulting theoretical predictions for the cross section. It can be shown[2] that if the broadening is of the resonant type, involving only the initial and final states of the optical transition, then the cross section for self-broadening will be

$$\sigma_{\mathrm{coll}}{}^{(1)}=\frac{4\pi}{15}\frac{r_0 c\lambda f}{\bar{v}_{12}}\ \mathrm{cm}^2,$$

whereas if the broadening is achieved primarily through intermediate states, then

$$\sigma_{\mathrm{coll}}{}^{(2)}=1.70\left\{\frac{e^4a_0{}^4}{\langle\Delta E\rangle_{\mathrm{av}}\hbar\bar{v}_{12}}\left[\frac{n^{*2}(n^*+1/2)(n^*+1)}{Z^{*2}}\right]^2\right\}^{2/5}\ \mathrm{cm}^2.$$

A by-product of our collision study was an accurate determination of the lifetime of the $^3P_1$ state which is of interest in the evaluation of data on atomic g values and nuclear moments[6] because it, together with the lifetime of the $^1P_1$ state which has also been measured for cadmium,[7] determines the mixing of the singlet and triplet states.[8]

The interesting phenomenon of coherence narrowing has been studied extensively in mercury and is expected to be closely similar in cadmium, although some of the assumptions of Barrat's theoretical work are not quite so well obeyed here as they are in mercury. Because of the onset of collision broadening it was not possible to observe the full predicted narrowing to three-tenths of the natural linewidth, as is predicted by the theory in the case of zero nuclear spin, but enough was seen to determine a substantial agreement between our results and Barrat's calculation.

In what follows, we discuss in Sec. II the basic results of the theory which are relevant to this study. In Sec. III, we give the details of the experimental method and techniques employed. In Sec. IV, the results of this study are presented together with some comments on the accuracy of the measurements, and finally in Sec. V we summarize briefly our results and compare them with other relevant measurements.

II. THEORETICAL PRELIMINARIES

The method of optical double resonance on which our work is based utilizes radio-frequency-induced changes in atomic polarization to determine the separation of Zeeman sublevels of an atomic state. In the case of cadmium ($I=0$ or $I=\frac{1}{2}$), the separation of these sublevels will be given by the diagonal elements of[9]

$$\mathcal{H}_{\mathrm{int}}=A\mathbf{I}\cdot\mathbf{J}+g_J\mu_e\mathbf{J}\cdot\mathbf{H}_0+g_I\mu_n\mathbf{I}\cdot\mathbf{H}_0,$$

where $\mathbf{H}_0$ is the static magnetic field (constant over the cell containing the cadmium atoms) and μ_e and μ_n are the electronic and nuclear magnetons, respectively.

In this work two cases are examined: (a) the $I=0$ isotopes in low static magnetic field, and (b) the $F=\frac{3}{2}$ level of the $I=\frac{1}{2}$ isotopes in fields so large that the level splittings become very different for the various magnetic sublevels, and any two adjacent sublevels may be considered as an isolated two-level problem insofar as induced radio-frequency transitions are concerned. Case (a) is a three-level problem, with the splittings given simply by $g_J\mu_eH_0$, where $\mathbf{H}_0$ is taken along the z axis. If an unequal distribution of excited state populations is produced by polarized optical radiation, then an applied radio-frequency magnetic field of the proper frequency will induce transitions among the various magnetic sublevels and, in general, change the population of these levels. This change is reflected in the number of optical photons detected in decay having a given polarization.[10] The method of the experiment described here is to excite only *sigma* transitions and to look for *pi* light in decay. An rf field of fixed frequency ω_0 is applied, and resonance is detected by sweeping the static magnetic field slowly through H_0, given by $\hbar\omega_0=g_J\mu_eH_0$, according to the above discussion.

For a system of equally spaced magnetic sublevels, Bitter and Brossel[1] have derived expressions for the resonance line shape by integrating the transition probability of Majorana[11] from $t=0$ to $t=\infty$, weighted by the probability of decay to the ground state, $(1/\tau)e^{-t/\tau}$, where τ is the lifetime of the excited state. The relevant quantity from the point of view of our experiment is the full width at half-maximum intensity of the resonance signal. However, in our case the matter is complicated by the problem of collisions with the walls. This means, in effect, that there is not an infinite amount of time available in which the atom can radiate, but that the time is limited by the time-of-flight to the walls. One can show[12] that for a spherical cell of diameter D, the half-width is given in the two cases of interest ($F=1$ and $F=\frac{3}{2}$) by

$$\Delta_{1/2}{}'^2(F=1)=\left(\frac{1}{\pi\tau}\right)^2\left(1+\frac{3\bar{v}\tau}{D}\right)+\frac{29}{5}\frac{(\gamma_FH_1)^2}{\pi^2}+\cdots,$$

$$\Delta_{1/2}{}'^2(F=3/2)=\left(\frac{1}{\pi\tau}\right)^2\left(1+\frac{3\bar{v}\tau}{D}\right)+\frac{(\gamma_FH_1)^2}{\pi^2}+\cdots,$$

through first order in $\bar{v}\tau/D$ and $(\gamma_FH_1\tau)^2$, where $\gamma_F=g_F\mu_e/\hbar$, H_1 is the magnitude of the rf field acting in the plane perpendicular to H_0, and $\bar{v}$ is the average velocity. In the above, and throughout this paper, a primed quantity will be one *not* corrected for wall col-

[6] P. Thaddeus and R. Novick, Phys. Rev. **126**, 1774 (1962); see also Ref. 4 above.
[7] A. Lurio and R. Novick, Phys. Rev. **134**, A608 (1964).
[8] A. Lurio, M. Mandel, and R. Novick, Phys. Rev. **126**, 1758 (1962).
[9] See, for example, G. W. Series, Rept. Progr. Phys. **22**, 280 (1959).
[10] W. E. Lamb, Jr., and T. M. Sanders, Jr., Phys. Rev. **119**, 1901 (1960).
[11] E. Majorana, Nuovo Cimento **9**, 43 (1932).
[12] F. W. Byron, Jr., thesis, Columbia University, 1963 (unpublished).

lisions. It is important to note that, for $\bar{v}\tau/D$ negligibly small, these expressions reduce to those of Bitter and Brossel,[1] and that as H_1 tends to zero the expression for the half-width is the same in both cases, namely

$$\Delta'_{1/2}=(1/\pi\tau)+(3\bar{v}/2\pi D).$$

Brossel and Barrat[13] demonstrated strikingly that τ as measured in a cell of atoms does not always correspond to the true radiative lifetime of a state, even at densities where collision broadening may be negligible. Barrat subsequently studied the problem of the radiation of an ensemble of N atoms theoretically and found that the true radiative lifetime τ was related to the measured lifetime or "coherence time" τ_c by

$$1/\tau_c=(1/\tau)(1-\alpha x),$$

where x is the probability that a photon emitted by an atom in the gas will be reabsorbed once before it escapes from the container. This is given by

$$x=1-\exp\{-(\pi/2)(r_0\lambda cf/\bar{v})nL\},$$

where L is a typical dimension of the container, λ is the wavelength, and f is the oscillator strength of the *optical* transition in question, n is the density in the cell, and r_0 is the classical electron radius. It should be emphasized that the factor L must be determined by fitting experimental data to the above formula. It must, of course, be of the order of magnitude of a typical cell dimension; α is related to the extent to which coherence is maintained in the radiative transfer process. It may be written

$$\alpha=\frac{1}{2F+1}\sum_{m=-F}^{+F}a_m\left[\frac{m^2-F(F+1)/3}{F^2-F(F+1)/3}\right],$$

where

$$a_m=\frac{21}{10}\sum_{\mu=-I}^{+I}|\langle 1,F-\mu;I,\mu|F,F\rangle \times\langle 1,F-\mu;I,m+\mu-F|F,m\rangle|^2.$$

The derivation of these results proceeds via the density matrix formulation. In such a calculation several assumptions are made. Primarily, the results depend on the hyperfine structure being well resolved with respect to the Doppler width of the optical line. In cadmium, where the Doppler width is about 1500 Mc/sec, the hyperfine splitting is about 6000 Mc/sec for both of the $I=\frac{1}{2}$ isotopes,[14] so that approximation is reasonably well obeyed here. Other assumptions are made by Barrat to simplify the computation. Their validity is discussed in a quite general manner in Barrat's paper.

As the cadmium density in the bulb is increased, after an initial narrowing because of the coherence effects mentioned above, the double resonance line will eventually begin to broaden under the influence of cadmium-cadmium collisions in which a ground-state atom interacts briefly at short range with an excited atom. The theory of the broadening of these magnetic dipole transitions is given in BF (see Ref. 2). It is shown that the velocity dependence of the self-broadening is different for allowed and partially forbidden optical transitions. If the oscillator strength is of the order of unity the self-broadening is velocity-independent and is given by

$$\Delta_{1/2}(\text{broadening})=n\bar{v}_{12}\sigma_{\text{coll}}^{(1)}/\pi,$$
$$\sigma_{\text{coll}}^{(1)}=(4\pi/15)(r_0\lambda cf/\bar{v}_{12}).$$

This has the typical Holtzmark form which results from assuming that the interaction is of the resonant type, that is, that it involves *only* the initial and final states of the optical transition. If the oscillator strength is sufficiently small, then the effect of the other atomic states may become relatively more important, and it is shown in BF that under these conditions the self-broadening is proportional to the three-fifths power of the velocity. In the particular case of a spin-zero isotope ($I=0$) it is found that this "second-order" self-broadening is given by

$$\Delta_{1/2}(\text{broadening})=n\bar{v}_{12}\sigma_{\text{coll}}^{(2)}/\pi,$$
$$\sigma_{\text{coll}}^{(2)}=A/\bar{v}_{12}^{2/5},$$

where $\bar{v}_{12}$ is the average relative velocity and

$$A=1.70\left[\frac{e^4a_0^4}{\langle\Delta E\rangle_{\text{av}}\hbar}\frac{n^{*4}(n^*+1/2)^2(n^*+1)^2}{Z^{*4}}\right]^{2/5}.$$

n^* and Z^* are Slater's[15] effective principle quantum number and effective nuclear charge for an electron in a $5s$ or $5p$ orbit of cadmium, and $\langle\Delta E\rangle_{\text{av}}$ is a mean excitation energy used to effect the above mentioned sum over intermediate states which arise in the theoretical evaluation of the cross section. When there is hyperfine structure present (i.e., $I\neq 0$) the situation is more complicated, although it is clear from the analysis in Ref. 2 that the cross section should be of the same order of magnitude as in the $I=0$ case. Observations on cadmium offer an excellent opportunity to observe these "second-order" collision cross sections, since $f=0.002$ for the ${}^1S_0$–${}^3P_1$ transition.

Although the above expressions for the half-width were derived under the assumption that $n\bar{v}_{12}\sigma_{\text{coll}}$ is much greater than the natural linewidth, it is natural to speculate that at any temperature the half-width can be adequately represented as a collision width plus a natural width narrowed by trapping. We write, therefore, including our correction for wall collisions which is certainly additive if the effect of wall collisions is

[13] J. P. Barrat and J. Brossel, Compt. Rend. **246**, 2744 (1958).
[14] R. F. Lacey, Ph.D. thesis, Massachusetts Institute of Technology, 1959 (unpublished).
[15] J. C. Slater, Phys. Rev. **36**, 57 (1930).

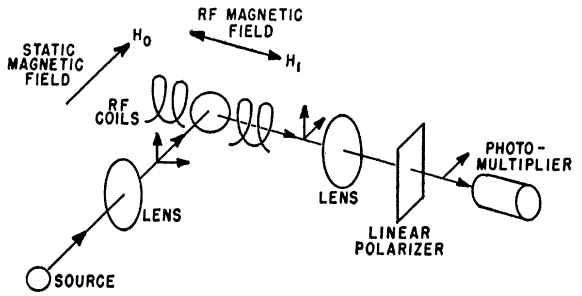

FIG. 2. Schematic drawing of the experimental arrangement.

small,

$$\Delta_{1/2}'(\theta)=\frac{1}{\pi\tau}(1-\alpha x)+\frac{n\bar{v}_{12}\sigma_{\text{coll}}}{\pi}+\frac{3\bar{v}}{2\pi D}$$

at zero radio-frequency field, where θ is the absolute temperature. This formula gives a rather accurate representation of the experimental data, although it should be remarked that the presence of an empirical length in the expression for x affords quite a bit of leeway in fitting the low-temperature region onto the high-temperature region, the latter being determined uniquely by a least-squares fit of the form

$$\Delta_{1/2}=\text{constant}+A[n\bar{v}_{12}{}^{3/5}/\pi]$$

in the density region where the coherence narrowing term attains its assymptotic value of $3/(10\pi\tau)$. The wall collision term here may be effectively regarded as a constant because of its very slight density dependence, i.e., because $\bar{v}$ varies only as $\theta^{1/2}$.

The postulate that the collision width and the natural width are additive has also been given experimental support by Piketty-Rives' measurements[16] on the broadening of double resonance lines in mercury by the noble gasses. There the broadening interaction definitely proceeds via intermediate states so that the situation is very similar to the one in cadmium. Piketty-Rives measured the cross section for foreign gas broadening at two distinctly different mercury densities, one at which no coherence narrowing should occur and the other at a higher density where there should be an appreciable amount of narrowing. Within the experimental error these two cross sections were the same for each of the noble gases, indicating that the coherence-narrowed natural width and the collision width are additive.

III. EXPERIMENTAL DETAILS

The experimental arrangement is shown in Fig. 2. Cadmium atoms were excited by focusing unpolarized light from an rf resonance lamp, of the type described in MN (see Ref. 4), through a system of quartz lenses onto an evaculated cell containing natural cadmium. The light was propagated along the direction of the static magnetic field, and hence only *sigma* transitions were excited in accordance with the discussion in Sec. II. Light scattered at right angles to the magnetic field was detected by a Dumont 7664 photomultiplier after travelling through a linear polarizer which was oriented to pass only *pi* light. A Schott UG-11 filter eliminated most of the strong visible and ultraviolet lines, except for the relevant intercombination line at 3261 Å. The scattering cell was situated in an aluminum oven with quartz windows, and the entire assembly was covered with an Alsimag lined copper heating hood, again with quartz windows. The heating was accomplished by a gas-oxygen flame directed through a hole in the ceramic base of the heating hood. Typical operating temperatures ranged between 140 and 340°C.

The rf magnetic field was applied by a single-turn square aluminum coil which surrounded the scattering cell. This produced an rf field perpendicular to the static field. Holes were cut in the coil in line with the windows in the oven and heating hood to admit the exciting radiation and permit the scattered radiation to be detected. Radio-frequency power of fixed frequency was supplied to the coil from a Hewlett-Packard model 608D VHF signal generator in conjunction with a pair of wideband amplifiers. Voltages up to 70 V could be obtained in this way, which produced rf magnetic fields up to 0.35 G, more than sufficient for the experiment in question. The rf was square wave modulated at 280 cps for the purposes of lock-in detection.

A. Scattering Cells

The scattering cells were generally spherical and from two to three centimeters in diameter. Sometimes cylindrical cells of about one inch in diameter and in length were used. After baking a cell under vacuum at 1000°C for 24 h, a small amount of distilled cadmium was admitted into the cell. Since pressures between 5×10^{-8} and 5×10^{-7} Torr were desired, an additional cleansing with a high-frequency discharge was carried out. The cells would then be pumped while at the same time the surface of the cell was sparked with a Tessla coil to drive off any residual contaminating foreign gas. Finally, when the cell pressure remained steady at about 10^{-7} Torr under sparking with the Tessla coil, the cell was sealed off from the pumping station.

To be certain that there was no foreign gas broadening initially, several cells were made which were connected directly to an ion gauge and barium *getter* via a long tube connected to the top of the cell, running through a specially constructed oven roof and out the chimney of our heating hood. At low cell temperature (about 150°C) the pressure measured with the ion gauge was consistent with the vapor pressure of cadmium at that temperature. Most of our half-width measurements at low density for determining the radiative lifetime were made with

[16] C. A. Piketty-Rives (unpublished).

these specially constructed cells. However, at high temperatures the diffusion rate of cadmium out of the cell and up to the ion gauge and *getter* became too great, and we were forced to determine the vapor pressure from the existing data on cadmium vapor pressure as a function of temperature. For this purpose, one end of a thermocouple was attached to the neck at the top of the cell where the metal was initially deposited. It previously had been determined that this was the coldest spot in the cell, and it was found after a high-temperature run that the metal always redeposited at this neck.

Considerable pains were also taken to determine the temperature gradients in the region in which the scattering cell was located. By positioning the thermocouple junction at various points around the cell after the system had been allowed to reach equilibrium under the influence of the gas-oxygen flame, temperature differences were found to be no more than two degrees. Temperature measurements made for determining the vapor pressure in the cell therefore are probably good to about a degree.

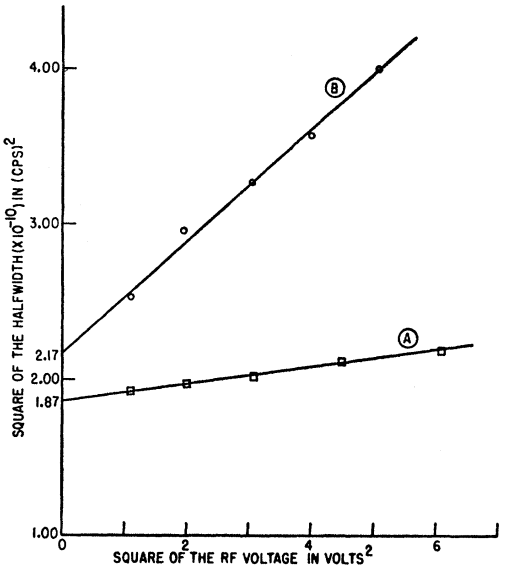

FIG. 3. Square of the half-width versus square of the rf voltage for the even isotope resonance. Curve A is for a 3.3-cm-diam cell, curve B is for a 1.1-cm-diam cell.

B. Static Magnetic Field

In order to avoid critical tuning of the rf circuit at different frequencies, the resonance is traced out by sweeping the static field through resonance according to the discussion of Sec. II. The static magnetic field is supplied by a pair of Helmholtz coils of 16-in. mean diameter, fed by a Harvey-Wells model HS-1050 magnet power supply. The sweep is provided by a motor-driven potentiometer, and the current is read on a Leeds-Northrup type K-3 universal potentiometer. Since measurements of linewidths were of primary interest, it was important that the static field be homogeneous over the central inch in which the cell rested. The half-width under investigation was about 130 kc/sec, and field broadening of less than 1 kc/sec was felt to be desirable. By careful adjustment of the Helmholtz pair, the variation of the static field over a central cubic inch was limited to $\Delta H_0 \cong 5$ mG for $H_0 = 500$ G. 130 kc/sec corresponds to a width of about 60 mG, for the $I=0$ case, in magnetic field units. If the field arose only from the coils, then $\Delta H_0 \propto H_0$, and ΔH_0 would equal about 0.2 mG at $H_0 = 20$ G, which is a typical operating region for the work on the even isotopes. This corresponds to about half a kilocycle of broadening. For the odd isotopes, the half-width is about 100 mG, and for typical operating conditions of $H_0 = 100$ G, $\Delta H_0 \cong$ mG, corresponding to about 1 kc/sec of broadening. The extreme variation over the whole volume is relevant here, since because of the fact that cadmium atoms move only about one millimeter during a lifetime, there will be no significant motional averaging. The above considerations assume that field gradients arise only from the coils. However, it is probable that there were also gradients associated with stray fields in the laboratory. If this were the case, then since g_F for the $I=0$ isotopes is $\frac{3}{2}$ and g_F for the $F=\frac{3}{2}$ level of the odd isotopes is unity, the effect of the stray fields on the broadening of lines in the even isotopes would be greater than that in the odd isotopes. However, as is shown in the next section, the measured natural widths of the resonance lines were equal to within experimental error for both isotopes. We believe that the field broadening is less than 1.0 kc/sec.

C. Sweep Effect

As was mentioned above, the magnetic field is varied linearly through resonance by a motor-driven potentiometer. The fact that we have a finite sweep time and a nonzero time constant associated with the circuit which integrates the signal from the lock-in detector will clearly result in a distortion of the resonance curves under observation. The dimensionless parameter which measures this effect is

$$\beta = \Delta_t \tau_{RC} / \Delta_{1/2} \tau_{SW},$$

where Δ_t is the total range of magnetic field swept through (in cps), centered about line center, τ_{RC} is the time constant of the integration circuit, τ_{SW} is the duration of the sweep, and $\Delta_{1/2}$ is the usual half-width (in cps) of the resonance curve. It can be shown[12] that for a Lorentz line shape, with center at ν_0, height at maximum $S_{\max}$ and half-width $\Delta_{1/2}$, these three quantities are altered according to

$$\tilde{\nu}_0 = \nu_0 \pm \Delta_{1/2}\beta,$$
$$\tilde{S}_{\max} = S_{\max}(1-4\beta^2),$$
$$\tilde{\Delta}_{1/2} = \Delta_{1/2}(1+6\beta^2),$$

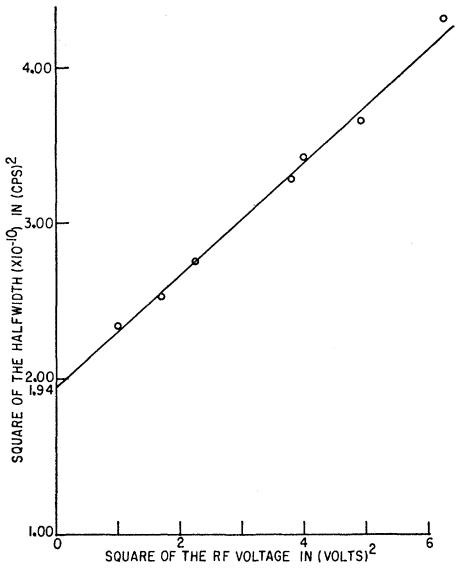

FIG. 4. Square of the half-width versus square of the rf voltage for the even isotope resonance using a cylindrical cell.

through the first nonvanishing order in β, and where a tilde denotes a quantity uncorrected for the sweep effect. The plus or minus sign depends in an obvious way on the direction of the sweep. In this work, Δ_t was approximately equal to three half-widths, and so if $\tau_{RC}=10$ sec and $\tau_{SW}=1125$ sec, then $\beta=1/38$, and the correction to the half-width will be less than 0.5%. These operating conditions were used throughout the experiment, thus effectively eliminating the problem of sweep distortion.

D. Optics

For the purpose of correcting for wall collisions, it is desirable to have the illumination as uniform as possible throughout the volume in which the cell rests.[12] This is achieved empirically by adjusting the position of the resonance lamp relative to the focusing lenses so that the light source images in the cell. Since the light sources are roughly the same size as the scattering cells and since the circular hole in the rf coil tends to function rather well as an aperture stop, this focusing is readily accomplished. Similarly, another hole in the coil, this one on the detection side of the apparatus, is just large enough to permit observation of effectively all of a spherical cell of the size used in this experiment. The coil is designed so that the scattering cell fits inside it with a minimum of space between cell and coil.

IV. RESULTS

A. Lifetime Measurement

Before an analysis of the collision-broadening phenomena can be made, an accurate knowledge of the natural, radiative lifetime of the $(5s,5p)$ $^3P_1$ state is necessary. Consider first the even isotopes. By working at sufficiently low temperatures ($T<160$°C), the effect of cadmium-cadmium collisions and also of coherence narrowing can be eliminated, and thus the natural linewidth is distorted only slightly by wall collisions and possible field inhomogenities. Making use of the relation $H_1=kV$, where V is the applied rf voltage and k is a constant depending on the geometry of the aluminum coil and on the frequency of the rf field, the half-width in the presence of rf is

$$(\Delta_{1/2}')^2=\left(\frac{1}{\pi\tau}\right)^2\left(1+\frac{3\bar{v}D}{D}\right)+\left(\frac{29\gamma^2k^2}{5\pi^2}\right)V^2.$$

Curve A in Fig. 3 is a plot of $(\Delta'_{1/2})^2$ versus V^2 for a bulb of 3.3-cm i.d. at 154°C. A least-squares fit gives for the intercept $\Delta'_{1/2}(V=0)=137\pm2$ kc/sec and the least-squares slope yields $k=1.6\times10^{-3}$ G/V.

Figure 4 shows the same relationship plotted for a run on a different coil. This time a cylindrical scattering cell was used. The results are $\Delta'_{1/2}(V=0)=139\pm2$ kc/sec and $k=5.8\times10^{-3}$ G/V. The half-width is seen to be in excellent agreement with the result for the spherical cell, but in this case it is difficult to correct accurately for the wall effect, although it is expected that the corrections will be a bit larger than in the spherical case. In this instance several consistency checks on the value of k were made. This was possible because of the relations,[1,12]

$$\gamma H_1{}^c\cong\sqrt{2}/4\tau, \text{ or } kV^c\cong0.011 \text{ G},$$
$$S=\sqrt{2}H_1\equiv kV,$$

where $H_1{}^c$ is the value of the rf magnetic field above which double peaking appears,[1] and S is the separation of the two peaks observed in the limit of very high rf fields where the dependence on H_1 is linear. Figure 5 shows a plot of S versus V at high rf voltages. From the slope, $k=5.5\times10^{-3}$ G/V. Also, V^c was determined roughly to be 1.8 V, from which we find $k=6.1\times10^{-3}$

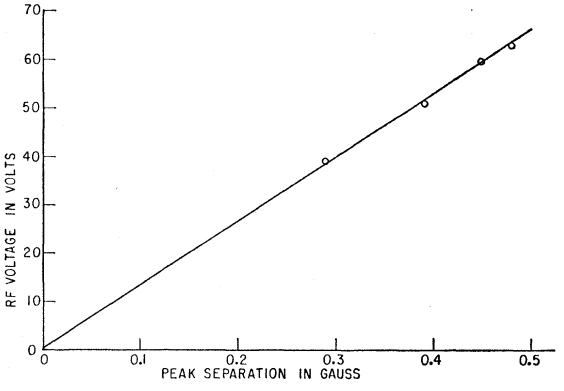

FIG. 5. Peak separation versus rf voltage for an $I=0$ resonance in the limit of large rf voltage.

G/V. Thus to within about five percent all these values for k agree.

To check the validity of the wall collision corrections, a series of observations was made with a small cell of 1.1-cm i.d. The result is shown in curve B of Fig. 3. The same aluminum coil was used as was used in the consistency measurements on k. In this case, $\Delta'_{1/2}(V=0)=147\pm2$ kc/sec, and $k=5.8\times10^{-3}$ G/V (in agreement with our other results for k discussed above). For $T=425°$K we find $3\bar{v}/2\pi D=14/D$ kc/sec. Hence the correction for the large bulb (Curve A of Fig. 3) is 4 kc/sec, while for the small bulb, the correction is 13 kc/sec. Hence for the large bulb, for the natural half-width in the absence of collisions, $\Delta_{1/2}=133\pm2$ kc/sec. For the small cell, $\Delta_{1/2}=134\pm2$ kc/sec. The agreement is excellent.

As a result of many measurements, a final value for the natural linewidth of $\Delta_{1/2}=133\pm2$ kc/sec was obtained. This leads to a radiative lifetime ($\tau=1/\pi\Delta_{1/2}$) of $\tau=(2.39\pm0.04)\times10^{-6}$ sec or to an oscillator strength[17] of $f=(2.01\pm0.03)\times10^{-3}$.

As was mentioned in Sec. III, to check on whether or not inhomogeneities were broadening the resonance lines, these same measurements were repeated for the $F=\frac{3}{2}$ level in the odd isotopes. By operating at sufficiently low rf voltages it was possible to suppress completely double-quantum transitions and achieve essentially a simple two-level situation. The only difficulty encountered here stemmed from the fact that the two $I=\frac{1}{2}$ isotopes have slightly different magnetic moments and hence different values of ω_0. This will appear as a slight broadening of a single resonance at low static fields, but at higher fields it is possible to split the two resonances corresponding to Cd^{111} and Cd^{113}. For this reason a cell of 95% Cd^{111} (1% Cd^{113}) was prepared. The results of a run on this cell are shown in Fig. 6, from which $\Delta'_{1/2}(V=0)=139\pm2$ kc/sec. The diameter of the cell used was 2.5 cm, and hence the formula for wall collision correction gives the natural half-width of the $F=\frac{3}{2}$ resonance as $\Delta_{1/2}=133\pm2$ kc/sec, in complete agreement with results on the even isotopes. This supports the estimates of Sec. III on the homogeneity of the static magnetic field.

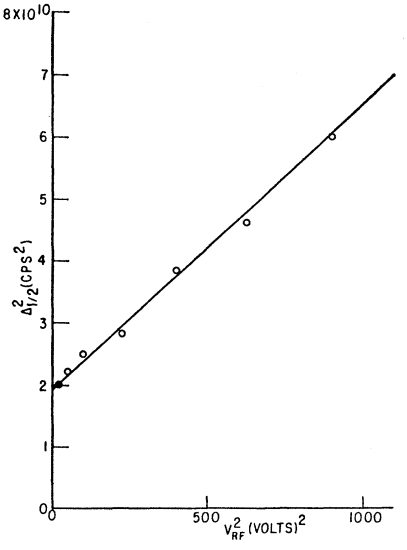

FIG. 6. Square of the half-width versus square of the rf voltage for the $m_F=3/2\rightarrow m_F=1/2$ resonance in 92% pure Cd^{111}.

[17] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, New York, 1961).

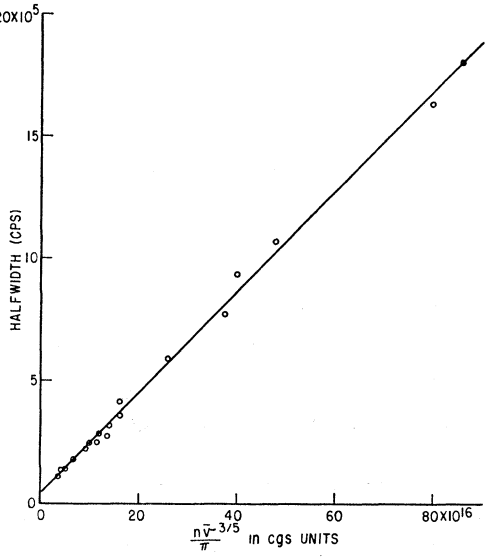

FIG. 7. The half-width of the $I=0$ resonance in natural cadmium as a function of $n\bar{v}_{12}{}^{3/5}/\pi$ in the high-density (linear) region.

B. Collision Broadening Measurements

It was suggested in Sec. II. that the density dependence of the half-width should have the form

$$\Delta_{1/2}=\frac{1}{\pi\tau}(1-\alpha x)+A\left[\frac{n\bar{v}_{12}{}^{3/5}}{\pi}\right]+\frac{3\bar{v}}{2\pi D}.$$

where x has a strong density dependence as pointed out in Sec. II and the velocity $\bar{v}$ has a very slight density dependence because it varies only as the square root of the temperature. Figure 1 shows a plot of the half-width of the $I=0$ resonance versus $n\bar{v}_{12}{}^{3/5}/\pi$ over the entire range of operating temperatures. The bulb contained natural cadmium. The curve is theoretical, fitted to the data by using a least-squares value of A obtained in the high-density region and by taking L, the adjustable parameter in x, to be equal to one centimeter. The points were obtained in two different cells over a time span of several months, indicating a high degree of reproducibility in the data. The agreement is seen to be good over the entire range, which suggests that the approximation that radiative and collision widths are additive

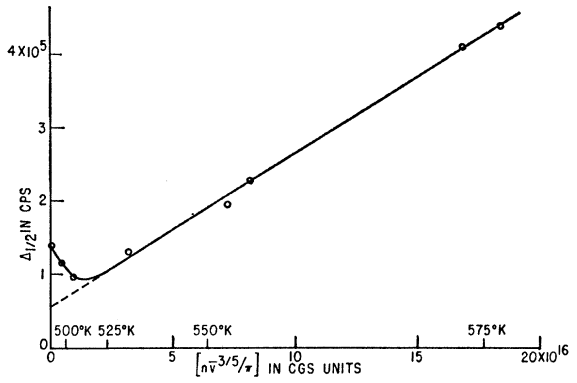

FIG. 8. The half-width of the $I=0$ resonance in 98% pure Cd^{114} as a function of $n\bar{v}_{12}^{3/5}/\pi$ in the high-density (linear) region.

is valid and verifies in a fairly quantitative way Barrat's theory of coherence narrowing in the case of cadmium.

Figure 7 shows a plot of the half-width of the $I=0$ resonance in natural cadmium versus $n\bar{v}_{12}^{3/5}/\pi$ in the high-density(linear) region of operation. The expected straight-line behavior is seen to be very well obeyed. A least-squares fit gives $A=(2.03\pm0.04)\times10^{-12}$ in cgs units, with an intercept of 47 ± 14 kc/sec. Figure 8 shows an identical series of measurements on a bulb of 98% pure Cd^{114}. Again the $I=0$ resonance was examined. In this case, $A=(2.09\pm0.03)\times10^{-12}$ in cgs units, with an intercept of 55 ± 9 kc/sec. Now on the basis of Barrat's theory, the coherence narrowed width of the natural line should be 40 kc/sec ($\alpha=7/10$ for $I=0$, $J=1$, as may be seen from our expression for α in Sec. II) and the mean value of the wall collision correction should be about 5 kc/sec over the region of operation, giving a total effective width at high temperature of 45 kc/sec apart from collision broadening. The agreement between the observed intercept and the theoretical value above is quite satisfactory. The two values of A show the same agreement, giving an average value of $A=(2.06\pm0.03)\times10^{-12}$ in cgs units. The agreement in these two cases suggests that the collision cross section is independent of whether or not the perturbing ground-state atoms have nuclear spin. This is to be expected on theoretical grounds.[2] To test this prediction in a more emphatic manner, the $I=0$ resonance was studied in a bulb of 92% Cd^{111} which contained roughly seven percent even isotopes. In this case almost all colliding ground-state atoms have nuclear spin. The resulting value of A was in complete agreement with those given above. (It is clear that the possibility of two excited-state atoms colliding can be neglected, since the fraction of excited-state atoms in the cell is $\phi\sigma_{\text{opt}}\tau=10^{-4}$, which is negligible. ϕ is the photon flux falling on the cell.)

The error assignments made above are based purely on the statistical spread of the data. However, there are several more important sources of error. For determining the density n from the measured temperature, the vapor pressure-temperature data of Landolt-Börnstein[18] was used, which gives

$$\log_{10}p=12.948-5906/\theta-0.2471\log_{10}\theta-0.0002696\theta.$$

Using the ideal gas law, this becomes

$$\log_{10}[n\bar{v}_{12}^{3/5}/\pi]=30.288-5906/\theta-0.9471\log_{10}\theta-0.0002696\theta,$$

where θ is the absolute temperature. The data from which the relation for $\log_{10}p$ is derived was taken largely in the temperature region in which we made our cross-section measurements, and it is expected to be quite accurate. However, it is clearly very sensitive to the temperature through the term in $1/\theta$. Although, as mentioned in Sec. III, the error in temperature measurement is probably no more than one degree, at a typical operating temperature of 550°K this results in a five-percent error in determining $n\bar{v}_{12}^{3/5}/\pi$. It is well known that in the alkali metals there is a further problem because the material interacts with quartz walls and the vapor pressure in the cell is affected correspondingly. It is not believed that cadmium does this to any appreciable degree, but to allow a margin of error we feel that an additional five-percent error here is not unreasonable, giving a total error spread of $\pm10\%$, introduced solely through the evaluation of the density.

Another source of error, which is very difficult to estimate, arises from the effect of absorption of the resonance radiation, which has heretofore been neglected. It is clear that as the density is increased the simple assumption of a uniformly excited Maxwellian gas starts to break down. Towards the center of the cell, for example, the atoms will see only the wings of the lamp profile (about three Doppler widths wide), and only those atoms will absorb radiation whose absorption lines are sufficiently Doppler shifted. This means that as the density increases the average velocity of the excited atoms will increase above the Maxwellian average towards the center of the cell. Thus $\bar{v}_{12}$ will not have the simple $\theta^{1/2}$ dependence which we have assumed throughout this work, but will have some density dependence. This in turn will give rise to an apparent increase in A because the $\theta^{1/2}$ dependence is assumed.

Fortunately, there are several factors which tend to reduce this "velocity selection" effect. First, the picture which one obtains by the most simple assumptions, namely, of a single photon scattering in the cell, is far too drastic. The situation is much more complicated, involving strong multiple scattering which will clearly reduce the effect. Second, the relative velocity is used, which involves averaging over *pairs* of atoms, one excited, one in the ground state. Since the velocity selection effect only operates on the components of the velocity of the excited atom in the direction of excitation

[18] *Landolt-Börnstein Tables*, edited by K. H. Hellwege (Springer-Verlag, Berlin, 1960), Vol. II, Part 2, Sec. a. See also K. K. Kelley, U. S. Bur. Mines Bull. 383 (1935).

and detection, this means that in computing the relative rms velocity, i.e.,

$$\bar{v}_{12}=\left[\int\int\int\int\int\int f_{1x}(v_{1x})f_{1y}(v_{1y})f_{1z}(v_{1z})f_{2x}(v_{2x}) \times f_{2y}(v_{2y})f_{2z}(v_{2z})(\mathbf{v}_1-\mathbf{v}_2)^2 d^3v_1 d^3v_2\right]^{1/2},$$

only two out of the six terms involved are affected by non-Maxwellian distributions. This is because $\bar{v}_{12}$ reduces to

$$\bar{v}_{12}=\left[\int_{-\infty}^{\infty} v_{1x}^2 f_{1x}(v_{1x})dv_{1x}+\cdots+\int_{-\infty}^{\infty} v_{2z}^2 f_{2z}(v_{2z})dv_{2z}\right]^{1/2}.$$

where the distributions are assumed symmetric about the origin. In a typical case, f_{1x}, f_{1y}, f_{1z}, and f_{2x} would be Maxwell distributions, while f_{2y} and f_{2z} would be altered by the velocity selection effect. Finally, the fact that $\bar{v}_{12}^{3/5}$ enters the equations as opposed to some higher power of $\bar{v}_{12}$ tends to further minimize the effect.

A very useful manifestation of this velocity selection effect, from the point of view of obtaining a quantitative estimate of its magnitude, was seen by measuring the line broadening as a function of the density in the manner previously described, except that by a series of stops and diaphragms the part of the cell nearest to the illuminated face was blocked off from the detection channel. This meant that those atoms which were sampled had a larger average velocity than those usually detected. In fact, an increase of about ten percent in the cross section was observed, which again tends to corroborate the suggestion that there is a velocity selection effect.

Aside from its quantitative value, the mere fact that this increase was observed is very interesting, for it shows that the broadening *does* depend on the velocity. In the case of true resonance broadening, as discussed in Sec. II, the broadening would be given by

$$\Delta_{1/2}(\text{broadening})=(4/15)r_0\lambda cfn,$$

which is independent of velocity. The fact that we do see an effect of the velocity on the broadening tends to verify that the dominant effect is not the resonant broadening which is velocity *independent*, but rather that the broadening is given by

$$\Delta_{1/2}(\text{broadening})=A\left[\frac{n\bar{v}_{12}^{3/5}}{\pi}\right],$$

which was obtained by assuming a second-order, nonresonant broadening process.

The above-mentioned figure of ten-percent increase in broadening is not unreasonable in light of studies which have been made of this problem using simplified models of the scattering process, and the previously mentioned value of $A=(2.06\pm0.03)\times10^{-12}$ in cgs units

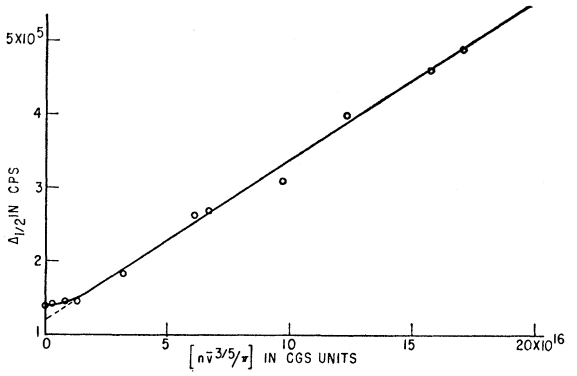

FIG. 9. Half-width of the $m_F=3/2\rightarrow m_F=1/2$ resonance in 92% pure Cd^{111} as a function of $n\bar{v}_{12}^{3/5}/\pi$ in the high-density (linear) region.

has been "corrected" by that amount. Because of the uncertainty involved in making this correction, half the correction is included in the error estimate. Thus the final experimental value for A, including also the estimated error in obtaining the density from the measured temperature, is $A=(1.85\pm0.28)\times10^{-12}$ in cgs units.

At this point, mention should perhaps be made of possible alterations of the wall collision correction. In obtaining that correction it was assumed[12] that the cell was uniformly illuminated, an assumption which clearly breaks down at sufficiently high density. For this reason, the following experimental test was made. A series of aperture stops was used to illuminate only a region of the cell removed by several millimeters from the walls of the cell ($\bar{v}_T\cong1$ mm) on the detection channel side. The cross section for collision broadening was measured again under these conditions and no significant difference in the result was found when compared with the number obtained under normal operating conditions. This suggests that wall collisions did not play an important part in the experiment.

Hence the cross section is given by

$$\sigma_{\text{coll}}=\frac{1.9\pm0.3}{\bar{v}_{12}^{2/5}}\times10^{-12}\text{ cm}^2,$$

where $\bar{v}_{12}$, as usual, is in cm/sec. This is to be compared with the value obtained theoretically from the expression of Sec II. Using $n^*=4$ and $Z^*=4.35$, which are the values of n^* and Z^* obtained for $5s$ and $5p$ electrons in cadmium according to Slater's rules,[15]

$$\sigma_{\text{coll}}{}^{(2)}=\frac{1.7\pm0.3}{\bar{v}_{12}^{2/5}}\times10^{-12}\text{ cm}^2.$$

This gives $\sigma_{\text{coll}}{}^2=2.5\times10^{-14}$ cm^2 at a typical operating temperature ($T=550$°K). It should be noted that at the same temperature $\sigma_{\text{coll}}{}^1=1.0\times10^{-14}$ cm^2, but this Holtzmark term, despite its comparable size, has virtually no effect on the *total* cross section, as shown in

BF. The error in the theoretical value is due to the necessarily rather crude method of evaluating certain sums and matrix elements which occur in second-order perturbation theory. The agreement is seen to be quite satisfactory.

The same measurements were made on the $m_F=\frac{3}{2}\rightarrow m_F=\frac{1}{2}$ transition in the $F=\frac{3}{2}$ level of 92% pure Cd^{111}. The results are shown in Fig. 9. The last-squares fit to the experimental data gives $A=(2.19\pm0.03)\times10^{-12}$ in cgs units with intercept 120 ± 10 kc/sec. In the case $J=1$, $I=\frac{1}{2}$, $F=\frac{3}{2}$, $\alpha=7/20$, and hence for the same reasons as in the case of $I=0$ resonances, the intercept should be only 92 kc/sec. This discrepancy is due perhaps to the breakdown of Barrat's assumption concerning the resolution of the hyperfine structure with respect to the Doppler width, which is not strictly obeyed here as was pointed out in Sec. II, and also to the fact that because of the high static fields used in this odd isotope case ($H_0=100$ G) the spacing of the m_F levels is no longer uniform.

After a correction of A for the velocity selection effect, σ_{coll} becomes

$$\sigma_{\text{coll}}=\frac{2.0\pm0.3}{\bar{v}_{12}{}^{2/5}}\times10^{-12}\text{ cm}^2.$$

This value agrees well with the value obtained for the $I=0$ case and with the theoretical $I=0$ value. The presence of hyperfine structure complicates the theory of pressure broadening considerably, and it is not possible to interpret this odd-isotope result except to say that one certainly would not expect any significant difference between the cross sections for the $I=0$ and $I=\frac{1}{2}$ cases.

V. DISCUSSION

The value of $(2.39\pm0.04)\times10^{-6}$ sec obtained for the radiative lifetime of the first $^3P_1$ state in cadmium is in excellent agreement with, although much more accurate than, earlier values quoted by Mitchell and Zemansky.[17] The average of their values is 2.43×10^{-6} sec. A recent measurement of the lifetime of the $(5s,5p)$ $^3P_1$ state of cadmium by the optical double resonance method has been reported by Butaux,[19] who finds a value of $(2.26\pm0.04)\times10^{-6}$ sec. However, since in his work no attempt was made to correct for the effect of wall collisions, some disagreement is to be expected. A correction to his value of the order of magnitude of the one used in this work would give agreement with our value, although since he used a cubical cell the correction will not have precisely the same value as the one used here.

As a result of examining the width of the cadmium double resonance line as a function of density, it was possible to verify Barrat's theory of coherence narrowing in a fairly quantitative manner, although the onset of collision broadening prevents a really detailed study of this effect in cadmium as opposed to the case of mercury where this effect has been examined in great detail.

The cross section for broadening was found to be, in the important $I=0$ case,

$$\sigma_{\text{coll}}=\frac{1.9\pm0.3}{\bar{v}_{12}{}^{2/5}}\times10^{-12}\text{ cm}^2$$

in good agreement with the theoretical calculation described in BF. This result, combined with similar studies in zinc,[20] gives considerable support to the interpretation of the results in the case of small oscillator strengths as a "second-order" phenomenon and to the theory of this effect.

ACKNOWLEDGMENTS

We would like to thank the staff of the Columbia Radiation Laboratory for helpful assistance in all phases of this work. One of us (FWB) would like to thank Columbia University for the grant of a Pfister and a Raytheon Fellowship and the National Science Foundation for a Summer Fellowship while this work was in progress.

[19] J. Butaux (unpublished).
[20] M. Dumont, thèse de troisième cycle, Paris, 1962 (unpublished).