Observation of the Line-Mixing and Collision-Time Asymmetry of the $5\,^1S_0 - 5\,^3P_1$ Line of the Even–Odd ^{113}Cd Isotope

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(Received February 25, 2004)

The profiles of argon perturbed components of the $5\,^1S_0 - 5\,^3P_1$ line of the even–odd ^{113}Cd isotope were measured using a laser-induced fluorescence method. It was shown that the asymmetries of the profiles are due to both the collision-duration and line-mixing effects.

PACS numbers: 32.70.–n, 33.70.–w, 34.20.–b

1. Introduction

The influence of the finite duration of collisions on the intensity distribution in pressure-broadened spectral lines has been the subject of numerous investigations [1–10]. These investigations have confirmed theoretical predictions that the first-order correction to the Lorentzian intensity distribution coming from the finite duration of collisions has a dispersion shape proportional to the collision duration time [11–14]. The resulting intensity distribution being the sum of Lorentzian and dispersion profiles appears to be asymmetric, and this line shape asymmetry is usually referred to as the collision-duration (CD) asymmetry.

On the other hand, there has been less work done on the spectral effects induced by line mixing due to quantum-mechanical interference between overlapping lines. The first theoretical treatments of the shape of pressure-broadened overlapping lines were given by Baranger [15], Kolb and Griem [16] and later were developed by Ben-Reuven [17] and others [18–21]. It was shown that at low densities of perturbing gas when the impact approximation is valid, i.e. when the collision time is assumed to be negligibly small, line mixing leads to asymmetric line shapes. This type of asymmetry is usually called the line-mixing (LM) asymmetry.

While the CD asymmetry has been observed both for atomic [1–10] and molecular [14] spectral lines, the LM asymmetry was found only for microwave and infrared as well as Raman spectra of molecules such as H_2, N_2, CO, CO_2, and others (cf. [20–22]).

To our knowledge, for atomic spectral lines in the optical region for the presence of line mixing no convincing experimental evidence has been demonstrated so far. However, we are aware of two existing theoretical attempts to infer the mixing of atomic spectral lines perturbed by neutrals. The first attempt was undertaken by Barklem et al. [23] who analyzed the selfbroadening of the hydrogen Balmer lines. Although they used the Baranger impact theory of pressure broadening of overlapping lines, they employed an approximation which in fact neglects the line-mixing asymmetry predicted by this theory. The second attempt was recently presented by Sanchez-Fortún Stoker and Dickinson [24] who applied the Baranger treatment of overlapping lines in their calculations of the intensity distribution of the sodium $3P-3D$ lines perturbed by atomic hydrogen. They focused their attention on the role of the line mixing in affecting the profile of the ${}^2P_{\frac{3}{2}}-3\,{}^2D_j$ doublet. Physically, in this case line mixing occurs due to collisionally-induced transitions between fine-structure $3\,{}^2D_{\frac{5}{2}}-3\,{}^2D_{\frac{3}{2}}$ levels and the presence of this effect is reflected in the line shape calculations in the existence of finite off-diagonal elements of the relaxation matrix. The calculated line shape was found to be asymmetric, but this asymmetry was shown to be a very small effect, too small to be observed in experiment or in solar absorption spectra. The main conclusion of calculations reported in Ref. [24] is that for sodium doublet $3\,{}^2P_{\frac{3}{2}}-3\,{}^2D_{\frac{3}{2},\frac{5}{2}}$ the mixing of the fine-structure levels has a negligible effect on the resulting profile of the doublet.

In the present work we have undertaken an experimental attempt to observe the line-mixing asymmetry in profiles associated with hyperfine-structure components of the atomic spectral line.

To this end we have chosen the intercombination line $5\,{}^1S_0-5\,{}^3P_1$ of the even–odd ^{113}Cd isotope. The $I=\frac{1}{2}$ nuclear spin causes hyperfine splitting of the upper state $5\,{}^3P_1$ into two $F'=\frac{1}{2}$ and $F'=\frac{3}{2}$ states separated by 0.2158 cm^{-1} [25]. As a result the intercombination line of this isotope consists of two hyperfine-structure components due to the $F'=\frac{1}{2}\longrightarrow F''=\frac{1}{2}$ and $F'=\frac{3}{2}\longrightarrow F''=\frac{1}{2}$ transitions with the intensity ratio equal to $\frac{1}{2}$. Here superscripts ($'$) and ($''$) refer to the upper and lower state, respectively.

In a series of previous papers from this laboratory [4–10] we reported results of precise measurements of the profiles of the $5\,{}^1S_0-5\,{}^3P_1$ intercombination line of the even–even ^{114}Cd isotope perturbed by various foreign gases. Measurements were made by means of the laser induced (LIF) method. The choice of the ^{114}Cd even–even isotope enabled us to avoid the hyperfine and isotopic structure of the 326.1 nm line. Obviously, no line mixing occurs in this case so our full attention in Ref. [4–10] was focused on the collision-time asymmetry as well as the asymmetry due to correlation between the Doppler and pressure broadening.

In the present work we report results of measurements of the shape of $5\,^1S_0 - 5\,^3P_1$ intercombination line of the even–odd ^{113}Cd isotope perturbed by argon. For the Cd–Ar system the ratio of the emitter and perturber masses is equal to 0.35 so that correlation between the Doppler and pressure broadening plays a negligible role in the formation of the resulting line shape and the only cause of the asymmetry of the profiles of the 326.1 nm line of the even–even ^{114}Cd isotope perturbed by Ar was identified in Ref. [6] with the finite duration of collisions.

Contrary to that, for the even–odd ^{113}Cd isotope perturbed by argon apart from the CD asymmetry, additional asymmetry should occur due to the mixing of the $F' = \frac{1}{2} \longrightarrow F'' = \frac{1}{2}$ and $F' = \frac{3}{2} \longrightarrow F'' = \frac{1}{2}$ hyperfine-structure components. The main goal of the present work was to verify the correctness of such an expectation.

2. Experimental apparatus

Measurements of the shape of the Cd 326.1 nm line were performed using side-arm quartz cells containing even–odd ^{113}Cd cadmium isotope and filled with argon situated in the special multisection oven enabling the independent temperature stabilization of the cell and its side-arm up to 1 K. During the measurement the temperature of the cell was kept constant at 724 K, while the side-arm was kept at a temperature of 440 K.

The experimental set-up is shown in Fig. 1. The line shape of the cadmium 326.1 nm line was registered using a substantially modified version of a digital laser spectrometer described elsewhere [26]. An actively stabilized single-frequency Coherent CR 899-21 ring dye laser equipped with an intracavity frequency doubler, operating on DCM dye was pumped by an INNOVA–400 argon-ion laser. The ring laser provided single mode UV output continuously tunable for up to 60 GHz with a line width of about 1 MHz. The intensity of the fluorescence signal was measured by a thermoelectrically cooled photomultiplier working in the photon counting mode. Frequency calibration of the ring laser was performed using its fundamental (red) line directed to a confocal Fabry–Perot interferometer (FPI) with a free spectral range of 1.5 GHz and the 100 cm long triple-pass iodine cell operated at temperature 35°C. Phase sensitive detection was employed to monitor the FPI peaks intensity and iodine spectrum. Two EG&G model 7260 DSP digital lock-in amplifiers were used in conjunction with Frequency Programmable EG&G 197 Light Choppers and silicon photodiodes. The FPI transmission peaks

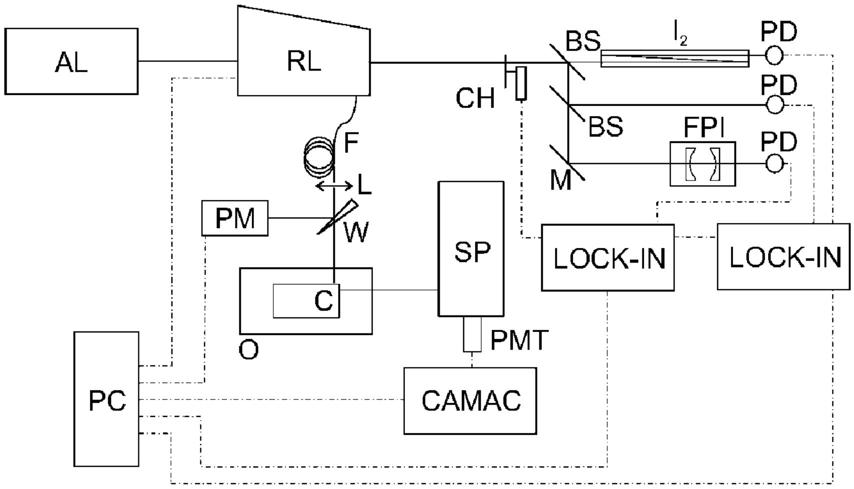

Fig. 1. The expetrimental set up: AL — ion argon laser, RL — ring dye laser with frequency doubler, F — fiber, L — collimating lens, W — beam splitting wedge, PM — laser power meter, O — oven, C — cell, SP — monochromator, PMT — photomultiplier, CAMAC — electronic system, BS — beam splitter, I_2 — triple-pass iodine cell, M — mirror, CH — light chopper, FPI — confocal Fabry–Perot interferometer, PD — photodiode, LOCK-IN — lock in amplifier, PC — computer, solid line — light beams, dash-and-dot line — electrical connections.

and I_2 absorption spectrum were recorded simultaneously with the fluorescence signal for frequency calibration. Photon counting was performed by an electronic system built in the CAMAC standard described elsewhere [27]. All the data: fluorescence signal, laser UV output power, FPI transmission peaks, and I_2 absorption spectrum were acquired with a PC computer for further evaluation.

3. Line shape analysis

In our earlier paper concerning the asymmetry of the 326.1 nm ^{114}Cd line perturbed by argon [6] we have shown that for the ^{114}Cd–Ar system the Doppler-collision correlation was negligible but the effects due to finite duration of collisions were strong enough to be detected by means of the LIF method.

As shown first by Anderson and Talman [11] and later discussed by several researchers [12–14] in the low pressure region the correction to the Lorentzian distribution coming from the finite duration of collisions has a dispersion form and the resulting line profile to be denoted by $I_{\mathrm{CD}}(\widetilde{\nu})$ of a group of nonoverlapping lines can be written as

$$I_{\mathrm{CD}}(\widetilde{\nu}) = \sum_{i,f} \frac{P_{if}}{\pi} \frac{(\gamma_{if}/2) + \chi_{if}(\widetilde{\nu} - \widetilde{\nu}_{if} - \Delta_{if})}{(\widetilde{\nu} - \widetilde{\nu}_{if} - \Delta_{if})^2 + (\gamma_{if}/2)^2}, \tag{1}$$

where the summation is over initial (i) and final (f) levels corresponding to the line with unperturbed frequency $\widetilde{\nu}_{if}$ and transition probability P_{if}. Here γ_{if} and $\Delta_{\rm if}$ denote the Lorentzian half-width and pressure shift for the $i \longrightarrow f$ transition, respectively. The assumption that the lines do not overlap is equivalent to that no line mixing occurs and χ_{if} can be really regarded as the measure of collision-time asymmetry. As was shown [1–14] χ_{if} is proportional to the density N of perturbing gas and $\kappa_{if} = \chi_{if}/N$ is referred to as the collision-time asymmetry coefficient. All three parameters γ_{if}, Δ_{if}, and χ_{if} can be expressed in terms of the elements of scattering matrix or time-evolution operators, respectively, suitably averaged over impact parameters and velocity. In the impact approximation, the collision-duration time is assumed to be negligibly small in comparison to the time between collisions and then $\chi_{if} = 0$ so that the resultant shape of the group of nonoverlapping lines is simply the sum of Lorentzian profiles.

On the other hand, when impact approximation is used in the case of overlapping lines for which line mixing occurs, then the line shape $I_{\rm LM}(\widetilde{\nu})$ can be written in the form [15–20]

$$I_{\rm LM}(\widetilde{\nu}) = \sum_j \frac{P_j}{\pi} \frac{(\gamma_{L_j}/2) + Y_j(\widetilde{\nu} - \widetilde{\nu}_j - \Delta_j)}{(\widetilde{\nu} - \widetilde{\nu}_j - \Delta_j)^2 + (\gamma_{L_j}/2)^2}, \tag{2}$$

where $\widetilde{\nu}_j$, γ_{L_j}, Δ_j, and P_j denote the unperturbed wavenumber, Lorentzian width, shift which contains the change of frequency due to the perturbation by neighbouring lines and the relative intensity of a particular line j, in the group of lines, respectively. In Eq. (2) Y_j denotes the line mixing parameter which vanishes for nonoverlapping lines.

Pine [20] has shown that the line mixing parameters summed over all coupled lines is zero, independently of the overlap or the magnitude of the line coupling elements. The Pine line-mixing sum rule has the form

$$\sum_j P_j Y_j = 0. \tag{3}$$

Comparing Eqs. (1) and (2) we can see that they are formally identical. In both cases the resulting profile of a group of lines is made up of a sum over symmetric Lorentzian shapes describing ordinary pressure broadening and shift and asymmetric dispersion profiles. However, the physical meaning of asymmetry parameters χ_j and Y_j in Eqs. (1) and (2) is completely different; χ_j depends on the collision-duration time and has nothing common with line mixing effects. Moreover, up to now experimental determinations of collision-time asymmetry have been made for isolated lines. In contrast with that Y_j depends on the collision-induced transition between various energy levels in the emitting atom and can differ from zero also in the impact limit, i.e. when collision-duration time is assumed to be equal to zero.

In two recent papers [28, 29] theoretical approaches have been developed which incorporate the problem of collision-duration into Baranger–Kolb–Griem treatment of line mixing. It was shown that in the first approximation the general formula for the line shape $I_{\text{LM-CD}}(\widetilde{\nu})$ which takes into account both the LM and CD effects can be written as

$$I_{\text{LM-CD}}(\widetilde{\nu}) = \sum_j \frac{P_j}{\pi} \frac{(\gamma_j/2) + M_j(\widetilde{\nu} - \widetilde{\nu}_j - \Delta_j)}{(\widetilde{\nu} - \widetilde{\nu}_j - \Delta_j)^2 + (\gamma_j/2)^2}, \tag{4}$$

where M_j is the total asymmetry parameter. In general case M_j can be expressed in terms of the diagonal and off-diagonal elements of the time-evolution operators for the initial and final states is a rather complicated way (cf. Eqs. (28) and (29) in Ref. [28]).

It should be noted that Eq. (4) has the same form as the asymmetric profiles given by Eqs. (1) and (2) of the "collision-duration only" and "line-mixing only" theories. In the general case, the total asymmetry parameter M_j cannot be represented by the sum of the parameters Y_j and χ_j since Y_j and χ_j are coupled through the off-diagonal elements of the time-evolution operators. Only in the case of weak-coupling of adjacent lines the total asymmetry parameter M_j can be expressed by a sum

$$M_j \approx Y_j + \chi_j\,. \tag{5}$$

Since our previous experiments on the Cd–Ar system indicated that in this case the correlation between the Doppler and pressure broadening can be neglected because of the small value (0.35) of the perturber-emitter mass ratio the resultant line shape formula $I_{\text{AV}}(\widetilde{\nu})$ that takes into account simultaneous occurrence of line mixing, collision duration, and Doppler broadening can be presented as a simple convolution of $I_{\text{LM-CD}}(\widetilde{\nu})$, Eq. (4) and the ordinary Gaussian profile $I_{\text{G}}(\widetilde{\nu})$:

$$I_{\text{AV}}(\widetilde{\nu}) = I_{\text{LM-CD}}(\widetilde{\nu}) \otimes I_{\text{G}}(\widetilde{\nu}). \tag{6}$$

The width of the Gaussian distribution of the j-th line is identified here with the pure Doppler width

$$\gamma_{\text{D}}^{(j)} = 2\sqrt{\frac{2kT\ln 2}{m_{\text{E}}}}\,\frac{\widetilde{\nu}_j}{c}, \tag{7}$$

where k, T, m_{E}, and c denote Boltzmann's constant, temperature, mass of the emitting atom, and speed of light, respectively.

Mathematically, the convolution in Eq. (6) is identical to the "asymmetric Voigt" (AV) profile first introduced in the context of the "collision-duration only" theory by Harris et al. [2] (cf. also [4–10]).

4. Results

As an example of the measured profiles, Fig. 2 shows the hyperfine-structure doublet $F' = \frac{1}{2}, \frac{3}{2} \longrightarrow F'' = \frac{1}{2}$ of the $5\,^3P_1 - 5\,^1S_0$ transition in the even–odd ^{113}Cd isotope perturbed by Ar at the pressure of 81 Torr at room temperature. As

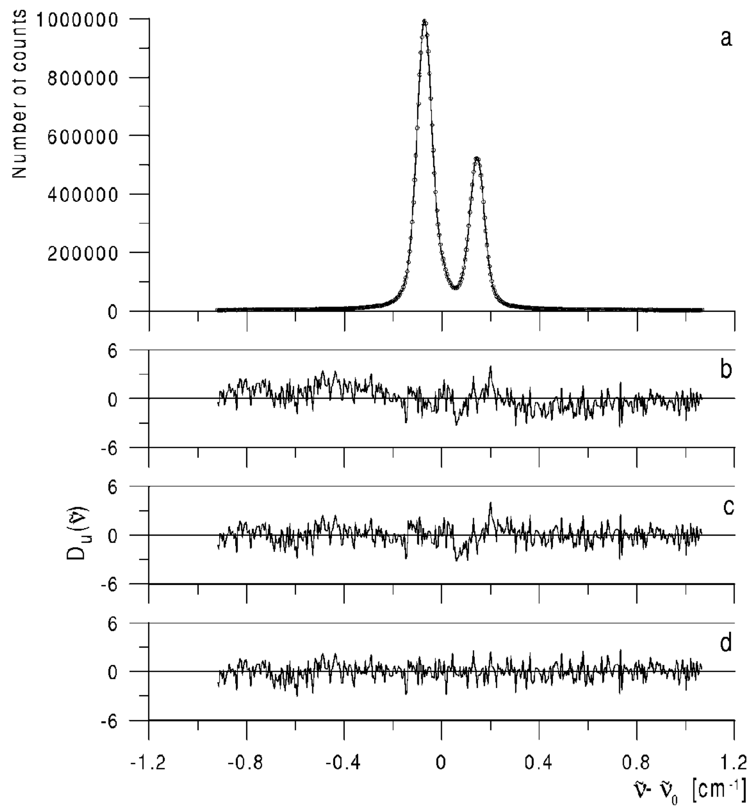

Fig. 2. The shape of the ^{113}Cd 326.1 nm line perturbed by argon at pressure 81 Torr: (a) experimental points together with the best-fit $I_{\rm AV}^{(\rm LM-CD)}(\tilde{\nu})$ profile taking into account both the collision-time and line-mixing asymmetries (full curve), (b)–(d) weighted differences $D_u(\tilde{\nu})$ between experimental and fitted: sum of two $I_{\rm VP}(\tilde{\nu})$ profiles, sum of two $I_{\rm AV}^{(\rm CD)}(\tilde{\nu})$ profiles (with the fixed value of collision-time asymmetry), and $I_{\rm AV}^{(\rm LM-CD)}(\tilde{\nu})$ profile, respectively.

in our previous study for Cd-noble gas atoms [4–10] we have used a least-squares algorithm for nonlinear parameters due to Marquardt [30] to perform the best-fit procedures. We have fitted our experimental profiles first to the pure Voigt profile (VP) in which neither CD nor LM effects are taken into account and then to the asymmetric Voigt profile (AVP) given by Eq. (6) in which CD is incorporated into LM effect. Since there are two hyperfine-structure components $F' = \frac{1}{2} \longrightarrow F'' = \frac{1}{2}$ and $F' = \frac{3}{2} \longrightarrow F'' = \frac{1}{2}$ (Fig. 2a) our experimental profiles were fitted to the sum of either two symmetric VP or two asymmetric Voigt profiles.

In order to examine the quality of the fits we used the weighted differences of the intensities

$$D_u(\widetilde{\nu}) = \frac{I_{\rm exp}(\widetilde{\nu}) - I_{\rm theor}(\widetilde{\nu})}{u(\widetilde{\nu})} \tag{8}$$

between experimental (measured) $I_{\rm exp}(\widetilde{\nu})$ and theoretical (fitted) $I_{\rm theor}(\widetilde{\nu})$ profiles, where $u(\widetilde{\nu})$ is the uncertainty of the measured signal. In Fig. 2b we can see systematic departures from zero in the line core as well as on line wings which can be regarded as a manifestation of the line asymmetry. We can also see the higher intensity in the red wing of this line, which is similar to the situation observed for Cd–Ar system [6] with ^{114}Cd isotope.

As the next step we have fitted the sum of two $I_{\rm AV}^{\rm (CD)}(\widetilde{\nu})$ profiles being calculated with the fixed value of collision-duration asymmetry parameter $\chi = -0.00106 \pm 0.00018$ resulting from our earlier measurements for ^{114}Cd [6]. As can be seen from Fig. 2c the systematic departures are still present in the line core, while on the line wings the quality of the fit is better. The departure due to the line asymmetry is lower because the $I_{\rm AV}^{\rm (CD)}(\widetilde{\nu})$ profile includes the collision-time asymmetry but not LM. We can thus conclude that in the case of the Cd–Ar system the collision-time asymmetry has a noticeable influence on the profile of the 326.1 nm ^{113}Cd line, but there is still another source of line asymmetry.

Finally, we have fitted the $I_{AV}^{\rm (LM-CD)}(\widetilde{\nu})$ profile (Eq. (6)) taking into account both the collision-duration and line-mixing asymmetry. As can be seen from Fig. 2d in this case the values of the differences are spread uniformly about zero which confirms the goodness of the fit. It is thus evident that in the case of the Cd–Ar system both the collision-time and line-mixing asymmetries have a noticeable influence on the profile of the 326.1 nm ^{113}Cd line.

From the best-fit procedure for the argon pressure 81 Torr we have determined the values of total asymmetry parameters M_j of both components to be $M_1 = -0.003322 \pm 0.00033$ for the $F' = \frac{1}{2} \longrightarrow F'' = \frac{1}{2}$ hyperfine component and $M_2 = 0.00270 \pm 0.00031$ for the $F' = \frac{3}{2} \longrightarrow F'' = \frac{1}{2}$ component. In order to deduce the values of the line-mixing parameters Y_j for these two components for collision-time asymmetry parameter we have taken the value $\chi = -0.00106 \pm 0.00018$ as determined in Ref. [6] for the ^{114}Cd isotope. Assuming the validity of the weak-coupling approximation from Eq. (5) we obtain the following values for the line-mixing asymmetry parameters: $Y_1 = -0.00216 \pm 0.00051$ for the $F' = \frac{1}{2} \longrightarrow F'' = \frac{1}{2}$ hyperfine component, and $Y_2 = 0.00376 \pm 0.00049$ for the $F' = \frac{3}{2} \longrightarrow F'' = \frac{1}{2}$ component. We should note that the ratio of intensities P_1/P_2 of the two components is equal to 2, and the values of Y_1 and Y_2 listed above which have opposite signs fulfil the sum rule, Eq. (3), due to Pine. This fact corroborates our assumption that the same value of the collision time asymmetry parameter $\chi_1 = \chi_2$ may be used for both hyperfine structure components. Moreover, the good quality of the fits shown in Fig. 2 may be regarded as an evidence that like the collision-time asymmetry also the pressure-broadening and shifting of particular hyperfine structure component of a spectral line are the same.

5. Conclusion

Using a LIF technique we have performed measurements of the profiles of two hyperfine-structure components $F' = \frac{1}{2} \longrightarrow F'' = \frac{1}{2}$ and $F' = \frac{3}{2} \longrightarrow F'' = \frac{1}{2}$ of the intercombination line $5\,^1S_0 - 5\,^3P_1$ of the even–odd ^{113}Cd isotope perturbed by argon at the pressure of 81 Torr. The profiles were found to be adequately described by the asymmetric Voigt profile. However, contrary to what was observed for the argon perturbed $5\,^1S_0 - 5\,^3P_1$ transition in the even–even ^{114}Cd isotope for the even–odd ^{113}Cd isotope the collision-duration effect itself cannot explain the observed asymmetry of the profiles. We have shown that for the ^{113}Cd isotope the observed asymmetry is due to simultaneous occurrence of both the collision-duration and line-mixing effects. The total asymmetry parameters M_1 and M_2 for both hyperfine-structure components have been determined and the line-mixing asymmetry parameters Y_1 and Y_2 have also been deduced assuming the validity of the weak-coupling approximation. These parameters were shown to fulfil the Pine sum rule. To our knowledge, measurements performed during the course of the present investigation provide the first evidence of the existence of line-mixing asymmetry in the atomic spectral line shape.

Acknowledgments

This work was supported by a grant No 5 PO3B 066 20 (354/PO3/2001/20) from the State Committee for Scientific Research.

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