



Quenching of Nal Fluorescence by H2, HCI, CO2, and H2O

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(2) No slowly decaying phosphorescence could be separated by the phosphoroscope.

Most organic substances which fluoresce also emit phosphorescence when in a rigid medium. This phosphorescence is always at longer wavelengths. It is, however, not surprising that such a phosphorescence was not found for azulene, because assuming a fluorescence-phosphorescence frequency difference⁵ of 2000- $10\ 000\ \mathrm{cm}^{-1}$, we find that the phosphorescent level of azulene would be above the lowest excited singlet level at 14 000 cm^{-1.3} A radiationless transition to the latter level could occur and, even if relatively slow, would compete against the highly forbidden triplet-

⁵ M. Kasha, Chem. Revs. 41, 401 (1947).

singlet transition which gives rise to the phosphorescence.

(3) No infrared emission was found when exciting with sodium yellow radiation.

Absence of infrared radiation corresponding to emission from the lowest excited singlet level suggests that the potential energy surfaces of the ground and the lowest excited singlet states intersect. It seems worth mentioning that all attempts to eke luminescence out of dimethyl fulvene were fruitless.

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Quenching of NaI Fluorescence by H_2 , HCl, CO₂, and H_2O^+

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The experimental quenching cross sections of H_2 , HCl, CO₂, and H_2O for the sodium D lines arising from the optical dissociation of the sodium iodide molecule have been determined by measurements with a photomultiplier tube. The velocities of the excited sodium atoms after dissociation of the sodium iodide molecules by ultraviolet light of different wavelengths have been determined by using an approximation for the repulsive potential curve of an excited sodium atom and normal iodine atom obtained from a measurement of the excitation of the sodium D lines as a function of exciting ultraviolet wavelength. The variation of quenching cross section for HCl and CO₂ with relative velocities of excited sodium atom and quenching molecules shows a decrease of cross section with increase in relative velocity. The cross section for H₂ shows little change with relative velocity in the range of velocities used. H₂O shows little quenching action. The source of ultraviolet light was a hydrogen discharge lamp and the wavelength of the exciting ultraviolet light in the 2100 A-2500 A range was controlled by a reflection grating monochromator.

I. INTRODUCTION

ERENIN¹ observed the optical dissociation of sodium iodide by ultraviolet light in 1926. The dissociation products² are normal or excited sodium and iodine atoms. The dissociation products to be considered are a sodium atom in the 3^2P state and a normal iodine atom. In returning to the ground state, the sodium atoms emit D light. Any excess energy that the ultraviolet photon possessed over that necessary to dissociate the sodium iodide molecule and excite the sodium atom goes into kinetic energy of the dissociation products.³ If an excited sodium atom engages in a collision of the second kind with a foreign molecule, it will not emit a D photon, and hence one might expect a quenching of the D lines fluorescence in the presence of foreign gases. The quenching cross section for this process has been measured for various gases and vapors by several investigators.^{4–7} Quenching of the D lines in resonance radiation experiments has also been studied.8-10 The source of ultraviolet light in past studies has been the spark lines of various metals. Little has been known about the relative efficiencies at different wavelengths in producing the D lines fluorescence from sodium iodide. The present study uses the continuous molecular spectrum of hydrogen as ultraviolet source and a monochromator to isolate narrow spectral regions. The relative intensities of D lines fluorescence have been measured as a function of exciting ultraviolet wavelength. From the data on the relative intensity distribution as a function of exciting wavelength, an experi-

[†] Supported in part by the Office of Ordnance Research.
¹ A. Terenin, Z. Physik 37, 98 (1926).
² H. D. Schmitt-Ott, Z. Physik 69, 724 (1931).
³ T. R. Hogness and J. Franck, Z. Physik 44, 26 (1927).

⁴ J. G. Winans, Z. Physik **60**, 631 (1930). ⁵ A. Terenin and N. Prileshajewa, Z. physik. Chem. **B13**, 72 (1931).

⁶Kisilbasch, Kondratjew, and Leipunsky, Physik. Z. Sow-jetunion 2, 201 (1932). 7 H. G. Hanson, Ph.D. thesis, University of Wisconsin, 1948

⁽unpublished). ⁸ R. G. W. Norrish and MacF. W. Smith, Proc. Roy. Soc.

⁽London) A176, 295 (1940). ⁹ L. V. Hamos, Z. Physik 74, 379 (1932).

¹⁰ R. Mannkopff, Z. Physik 36, 315 (1926).

mental plot of the potential curve for sodium in the 3^2P state together with an iodine atom in the ground state has been constructed. With a knowledge of the upper repulsive state for the excited sodium atom together with an iodine atom, one can ascertain for all wavelengths of exciting ultraviolet light the relative kinetic energy of separation of the dissociation products due to the excess ultraviolet photon energy. Thus, it is possible to determine the dependence of quenching cross section on the relative speeds of excited sodium atoms with respect to quenching molecules.

II. EXPERIMENTAL

The experimental arrangement is shown in Fig. 1. The sodium iodide salt is placed in a 15 mm diameter Vycor tube which has a fused quartz side window. The tube is approximately 15 cm long with the side window equidistant from the ends. The tube is mounted vertically inside an electric furnace and attached to the vacuum system by a quartz to Pyrex glass seal. Figure 1 shows the top view of furnace and tube. The Nichrome wound furnace is cylindrical in shape and furnished with four viewing windows as shown. The furnace is closed at top and bottom. The windings are so arranged that the central portion of the furnace is at the highest temperature even if the four central windows allow considerable radiation cooling.

When the salt is heated under vacuum, some of it sublimes from the position in the Vycor tube below the windows to a cooler portion of the furnace above the windows, forming a porous plug of condensed salt in the upper portion of the tube. This porous salt plug prevents further rapid loss of salt from the tube. After long heating, an equilibrium arrangement of the two salt surfaces is attained, both surfaces being at the same temperature. This method dispenses with the necessity of using ground quartz stops as were found necessary by previous investigators.^{4,5,7}



FIG. 1. Arrangement of apparatus.

The temperature of the furnace is held constant by a modified Wheelco temperature control to within $\pm 1^{\circ}$ C. The temperature is measured with a Chromel *P*-alumel thermocouple and a potentiometer.

The ultraviolet light source is a water-cooled hydrogen discharge lamp obtained from the Hanovia Chemical and Manufacturing Company. The lamp operates on a 5000 volt ac source at approximately $\frac{1}{2}$ amp. The lamp was monitored by a Photronic cell arrangement. The ratio of visible light output of the lamp as measured by the Photronic cell and the *D* line fluorescence intensity produced by the ultraviolet output of the lamp always remained constant even though the lamp's total intensity decreased with time as it heated when put in operation.

The monochromator is a Bausch and Lomb 500 mm focal length reflection grating instrument with a 100 mm \times 100 mm grating area and a dispersion of 16.5 A per mm in the first order. The grating is blazed for ultraviolet in the first order. The slit width used is 3.0 mm, corresponding to a 50 A spread in exciting wavelength at any setting.

The ultraviolet light was brought to a focus in the sodium iodide fluorescence tube by a quartz lens, as shown in Fig. 1. An image of the cone of fluorescent light in the tube is imaged on a slit by a glass lens. Behind the slit is a multi-layer filter with peak transmittance for the D lines. The fluorescent light then falls on the 1P21 photomultiplier tube of a Photovolt Corporation photometer. The amplified current output of the photometer operates a G.E. reflecting galvanometer attached to the monochromator. The light beam from the reflecting galvanometer falls on photographic paper wound on an extension to the wavelength drum of the monochromator. The trace on the photographic paper then corresponds to the intensity of fluorescence as a function of exciting ultraviolet wavelength. Reference marks are put on the photographic paper for various wavelength settings of the drum before a trace is recorded. The wavelength drum is turned by a synchronous motor during the recording of the trace.

Measurements were made by drawing a base line and a smooth curve through the trace by eye and measuring the amplitude of the trace with a rule for a series of equispaced wavelengths. The average of measurements on 5 or 10 traces was used to determine the intensity of fluorescence at any exciting wavelength.

Quenching gas pressures were measured by a mercury manometer. A McLeod gauge and a Pirani gauge were used at low pressures. The gases used were of reagent quality obtained from the Air Reduction Sales Company.

III. RESULTS AND INTERPRETATION

The quenching cross section calculations are similar to those of Terenin and Prileshajewa.^{5,11} If one assumes ¹¹ N. Prileshajewa, Physik. Z. Sowjetunion 2, 351 (1932); 2 367 (1932).



FIG. 2. I_0/I is the ratio of unquenched to quenched fluorescence. The data for H₂ and H₂O shown here was taken without the monochromator but using the total ultraviolet output of the hydrogen discharge lamp. The data for CO₂ and HCl is the average of I_0/I for all exciting wavelengths selected by the use of the monochromator.

that every collision between an excited sodium atom and a quenching molecule is a quenching collision, the Stern-Volmer relation can be stated

$$I/I_0 = 1/(1+z\tau)$$
 (1)

where I/I_0 is the ratio of quenched to unquenched fluorescence, τ is the mean life time of the excited state of the atom and z is the expected number of collisions per second for the excited atom. Let the gas kinetic expression¹² for z be:

$$z = \pi^{\frac{1}{2}} n \sigma^2 \alpha \psi(x) / x, \qquad (2)$$

where *n* is the number of quenching molecules per cm³; $\pi\sigma^2$ is the quenching cross section; $\alpha = (2RT/M_Q)^{\frac{1}{2}}$, the most probable speed of quenching molecules (M_Q) is the molecular weight of the quenching gas molecules); $v_{Na'}$ is the most probable speed of the excited sodium atoms; $x = v_{Na'}/\alpha$; and

$$\psi(x) = x \exp[-x^2] + (2x^2+1) \int_0^x \exp[-y^2] dy.$$

The most probable speed of the excited sodium atom, $v_{Na'}$, is calculated by the relationship

$$v_{Na'} = v_1 + \frac{1}{3} v_{NaI}^2 / v_1 \quad \text{for} \quad v_1 > v_{NaI}$$
$$v_{Na'} = v_{NaI} + \frac{1}{3} v_1^2 / v_{NaI} \quad \text{for} \quad v_{NaI} > v_1$$

where v_1 is the speed of the excited sodium atom relative to the sodium iodide molecule from which it came, and $v_{NaI} = (2RT/M_{NaI})^{\frac{1}{2}}$. From elementary considerations

$$v_1 = \left[2wm_I m_{Na}^{-1} (m_I + m_{Na})^{-1} \right]^{\frac{1}{2}}, \tag{3}$$

where w is the excess energy of the exciting ultraviolet photon over the energy needed to dissociate the sodium iodide molecule and excite the sodium atom. Eliminat-

¹² L. B. Leob, *The Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1934), 2nd edition, p. 102.

ing z between Eq. (1) and Eq. (2) and accounting for the number of quenching molecules per cm^3 at different pressures and temperatures one obtains

$$\sigma^{2} = \left[\frac{1.04 \times 10^{-19} T}{\pi^{\frac{1}{2}} \tau \alpha} \cdot \frac{x}{\psi(x)}\right]^{(I_{0}/I - 1)}_{P_{MM}}, \qquad (4)$$

where P_{MM} is the pressure of the quenching gas in mm Hg. Denoting the quantity in brackets in Eq. (4) by 1/K, one obtains

$$I_0/I = K\sigma^2 P_{MM} + 1.$$
 (5)

The value of K is fixed by choice of quenching gas, operating temperature, exciting ultraviolet wavelength and knowledge of the mean life of the excited state of the sodium atom. The value of τ was taken as 1.61×10^{-8} sec.¹³

From Eq. (5), it can be seen that if the Stern-Volmer relation holds a plot of I_0/I vs P_{MM} should yield a straight line with intercept of unity. Figure 2 shows the average values of I_0/I for all wavelengths of exciting ultraviolet light vs P_{MM} for the quenching agents used. It is to be noted that not all curves pass through 1.00 at zero pressure. The curves drawn are the best curves in the sense of "least squares." The failure to pass through 1.00 is apparently the result of an uncertainty in the observed value of I_0 .

The uncertainty in I_0 was investigated. Figure 3 shows a curve of I/I_0 for small pressures of hydrogen which is a moderate quenching agent. An enhancement of fluorescence is observed during the increase of hydrogen pressure from zero to approximately 2 mm Hg. This enhancement was also observed for water vapor as quenching agent. The assumed explanation of this enhancement is that the distribution of the sodium



FIG. 3. The enhancement of NaI fluorescence by the addition of small pressures of a weakly quenching gas. A similar result was observed for H_2O as a quenching agent.

¹³ G. Stephenson, Proc. Phys. Soc. (London) A64, 458 (1951).



FIG. 4. The intensity of D line emission following the optical dissociation of the NaI molecule by ultraviolet light as it depends on the wavelength of the exciting light for two different temperatures of NaI salt vapor.

iodide salt vapor density in the fluorescence tube changes during the transition from pressures where the mean free path is of the order of magnitude of the dimensions of the fluorescence tube to mean free paths that are small compared to the dimensions of the fluorescence tube. The vacuum attained during the measurement of I_0 was about 10^{-5} mm. Hg under optimum conditions. However, a certain amount of free iodine was always observed in the traps of the system after the salt had been heated for some time. The exact residual pressure due to this iodine vapor as well as the vapor pressure of the sodium iodine itself at various operating temperatures was unknown. Since the measured value of I_0 is subject to uncertainty, it was considered that the trend of the I_0/I curves for quenching pressures larger than 2 mm Hg would determine the experimental slope to be used together with Eqs. (4) and (5) to determine the value of σ^2 . A "least squares" determination of the best straight line representation of I_0/I vs P_{MM} was made for every exciting ultraviolet wavelength. The value of P_{MM} corresponding to $I_0/I=2$ (irrespective of whether the curve passes through 1.00 at $P_{MM}=0$) was used to calculate σ^2 from Eq. (4), While this method is not exact, it minimizes the effects of errors in measurement of intensity of fluorescence at very low or very high quenching pressures and gave the most consistent results over different runs on the same quenching agents. Attempts to determine the "correct" value of I_0 by extrapolating to zero quenching pressure, using only data from higher quenching pressures, gave results which were less consistent between successive runs. This was probably due to the sensitivity of such a procedure to errors in measurement of the low values of I corresponding to high quenching pressures. A consideration of the error introduced by the method of treating the data will show that the values of σ^2 calculated may tend to be somewhat lower than their true values.

The measurement of intensity of unquenched fluorescence as a function of exciting wavelength necessitated a measurement of the intensity distribution of the source as a function of wavelength. The calibration of the hydrogen lamp together with the monochromator was accomplished by placing a sodium salicylate coated plate at the exit slit of the monochromator. The fluorescent response of the sodium salicylate was measured with the photometer. The response of a 1P21 photomultiplier tube to the fluorescence of sodium salicylate excited by ultraviolet light has been shown to be proportional to the number of exciting ultraviolet photons.¹⁴ A thickness of quartz, approximately the same as that involved in the quenching apparatus, was placed between the sodium salicylate coated plate and the photomultiplier tube to equalize the optical paths during the calibration and the fluorescence measurements.

Figure 4 shows the relative intensity of sodium Dlines fluorescence as it depends on exciting ultraviolet wavelength. The curves have been corrected for the characteristics of the source and, therefore, their shape should depend only on the properties of the sodium iodide molecules at the temperatures of measurement. Four experimental runs at intermediate temperatures gave curves which were intermediate between the extremes shown. The curves are normalized at their maxima. Since the slit width used corresponded to 50 A, it is not considered that the shift in maximum at the two temperatures is real. However, the onset of fluorescence approaching from the long wavelength side depends markedly on the temperature. A greater change in onset wavelength with temperature was observed by Visser¹⁵ in the case of thallium iodide. A measurement on sodium iodide under unknown conditions by Prileshajewa¹⁶ shows an onset wavelength of 2500 A and a maximum at 2380 A. Terenin and Prileshajewa⁵ give 2430 A as the onset wavelength.

The upper repulsive state, as shown in Fig. 5 for sodium in the 3^2P state together with iodine in the ground state, was approximated in the following way: The lower potential curve for the sodium iodide molecule in the ground state is a Morse curve calculated from constants for sodium iodide listed by Herzberg.¹⁷ The first eight vibrational levels are shown. The 3 mm slit on the monochromator corresponds to approximately 1000 cm⁻¹ spread in the energy of the ultraviolet beam for any setting of the monochromator in the range used. This corresponds to the spacing of three or four vibrational levels so it is not possible to resolve

¹⁴ K. Watanabe and Edward C. Y. Inn, J. Opt. Soc. Am. 43, 32 (1953).

¹⁵G. H. Visser, thesis, Delft, 1932 Table 43 in P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949), p. 212.

¹⁶ Presented in Fig. 8, p. 335 [J. M. Frank, Physik. Z. Sowjetunion 2, 319 (1932)].

¹⁷ G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand Company, Inc., New York, 1950), 2nd edition, p. 555.

the contributions to the fluorescent intensity from individual vibrational levels. At the temperatures used, only the first seven or eight levels contribute significantly to the fluorescent intensity. The Franck-Condon principle in its simplest form was used together with the Boltzmann temperature distribution to calculate an approximation for the upper repulsive curves shown in Fig. 5. It was assumed that transitions directly upward occurred only at the turning points of vibrational states and were equally likely from either end of a vibrational state. Also that the number of upward transitions from any vibrational state was proportional to the population of that state. In Fig. 5, the relative Boltzmann populations of the vibrational states for two different temperatures are shown each individually referred to 100 percent for the zeroth level. The two upper repulsive curves calculated from the data taken at the two temperatures were obtained by plotting points directly above the ends of each vibrational level. The distance above the end points of the vibrational levels was obtained by noting the wavelength of exciting light in Fig. 4 corresponding to the percent of intensity expected from each level in terms of its relative population. (It was assumed that transitions upward from the center of the zeroth vibrational state were responsible for the maximum intensity of fluorescence and that the upper curve was



FIG. 5. The repulsive potential curve for the excited sodium atom together with a normal iodine atom as deduced from the data in Fig. 4. The lower potential curve is a Morse curve constructed from known constants of the NaI molecule.



FIG. 6. Curve A is the observed intensity. Curve B is the calculated intensity which is the sum of the intensities obtained from considering the probability density functions of the first seven vibrational states of the sodium iodide molecule.

a repulsive curve with no minima.) The fact that the curves for the two temperatures do not coincide indicates to some degree the error in the measurements and in the assumptions themselves. The maximum separation of the two curves is approximately one-half the energy interval corresponding to the slit width used in the experiment.

The potential curve obtained by the foregoing severely simplifying assumptions was investigated by the application of more conventional methods. Using the upper potential curve of Fig. 5 and the vibrational eigenfunctions of the first seven vibrational states of the sodium iodide molecule, a calculation of the expected distribution of intensity of fluorescence was made. The method used is similar to the methods discussed.¹⁸

The probability density distribution functions used were those of a harmonic oscillator calculated from the constants given for sodium iodide.¹⁷ The probability density distribution curves were drawn to scale so that the classical turning points for each vibrational level coincided with the intersection of that vibrational level with the lower potential curve in Fig. 5. The difference between the Morse curve used and the true parabola one would have for a harmonic oscillator was small enough for the first seven vibrational states so that the same scale factor could be used for all seven probability density functions.

The contribution of each vibrational level to the total expected intensity was obtained by a "reflection" of the probability density function for each level from the upper curve.¹⁷ The ν factor,¹⁹ was omitted because the intensity of fluorescence observed depends only on the number of photons involved in transitions and not on the energy of each exciting ultraviolet photon. The contribution of each vibrational level to the intensity of fluorescence is shown in Fig. 6. Each level's contribution has been adjusted by the appropriate Boltzmann temperature factor. The calculations of

¹⁸ See reference 17, p. 391.

¹⁹ See reference 17, p. 393.



FIG. 7. The ratio of quenched to unquenched NaI fluorescence intensity for different wavelengths of exciting ultraviolet light for different quenching agents.

the "reflected" curves were done graphically. The calculations were made for the 668°C data only.

Curve B in Fig. 6 is the total intensity from the zeroth through the sixth vibrational level obtained by summing up the contributions from the individual states. Curve A is the observed fluorescent intensity distribution from Fig. 4 plotted against exciting ultraviolet energy expressed in cm⁻¹. It will be noted that a much better apparent agreement between curves B and A could be achieved by moving B about 500 cm⁻¹ toward lower wave numbers (i.e., lower every point on the upper potential curve in Fig. 5 by 500 cm⁻¹). However, if one considers that, had the true (anharmonic) probability density functions for the sodium iodide molecule been used, curve B would be relatively higher at lower wave numbers and lower at higher wave numbers. This would be so because the loops in the anharmonic probability density functions would be larger on the side of r_e corresponding to larger internuclear distances. This modification of curve Bby using the anharmonic probability density functions would probably give a fair agreement with the observed intensity curve A. For the determination of w [Eq. (3)] the potential curve in Fig. 5 was taken as an approximation to the upper potential curve for the sodium iodide molecule.

Two possible asymptote levels for large internuclear separation of the sodium iodide molecule for the upper state are shown in Fig. 5. The two levels are calculated from dissociation energies for the ground state of sodium iodide of 3.16 ev and 3.00 ev taken from spectroscopic data listed by Herzberg¹⁷ and Terenin's^{1,5,20} work on the optical dissociation of sodium iodide, respectively. Thermochemical data gives 3.07 ev. If the correct value is 3.16 ev, the possibility of a slight minimum in the upper potential curve exists. An asymptote at 42 100 cm⁻¹ was assumed in the calculation of w, the excess energy of the dissociation partner.

The minimum value of w [Eq. (3)] for each exciting wavelength was determined from Fig. 5 in the following way. A vertical distance in cm⁻¹ corresponding to an exciting wavelength was moved with its lower end on the lower potential curve until the upper end was on the upper repulsive curve. This point on the upper repulsive curve, together with the assumed asymptote for the repulsive curve for large internuclear distance of 42 100 cm⁻¹, determines w. The vertical distance between this point for each exciting wavelength and 42 100 cm⁻¹ is a measure of w, the minimum excess kinetic energy shared by the dissociation partners for that particular exciting wavelength. The value is a minimum because upward transitions for the same wavelength originating in a point between the classical turning points for each vibrational level (corresponding to loops in the probability density functions between the classical turning points) could end further up on the upper repulsive curve yielding a larger value for w.

Figure 7 shows the quenching data on the quenching agents used, as a function of wavelength of excitation of fluorescence. The only agent to show a definite dependence on exciting wavelength is HCl.

²⁰ K. Butkow and A. Terenin, Z. Physik 49, 865 (1928).



FIG. 8. The quenching cross sections are plotted against the most probable relative velocities between excited sodium atoms and quenching molecules.

Figure 8 shows the quenching cross section $\pi\sigma^2$ for the various quenching agents as calculated from Eq. (4) plotted against V_R , the average relative velocity of approach between excited sodium atoms and quenching molecules.

 V_R is calculated from $V_R = v_{Na'} + \frac{1}{3}\alpha^2 / v_{Na'}$ for $v_{Na'} > \alpha$ and $V_R = \alpha + \frac{1}{3} v_{N\alpha'}^2 / \alpha$ for $\alpha > v_{N\alpha'}$. Since the light hydrogen molecules have average thermal velocities which are greater than the excited sodium atom velocities and since hydrogen is a relatively poor quencher, it is not surprising to see little dependence of the quenching cross section for hydrogen on V_R over the small range of V_R covered. It should be kept in mind also that the actual relative velocities involved in individual collisions vary from zero to several times V_R due to the Maxwellian distribution of speeds of the quenching molecules. The calculated cross sections for HCl and CO₂ show about the same relative decrease with increasing V_R in spite of the fact that HCl was the only one of the two to show a dependence of the measured I_0/I on the wavelength of the exciting ultraviolet light.

The quenching cross sections for H_2 and CO_2 from Winans⁴ data and for H_2 from the resonance D line quenching experiments of Norrish and Smith⁸ have been recalculated by the above method and are shown in Fig. 8.

In conclusion, it appears that for HCl and CO_2 and also for H₂ (considering the value of cross section at low relative velocities obtained by Norrish and Smith⁸) that the efficiency of quenching of the sodium *D* lines decreases with increasing of average relative velocity of approach between excited sodium atoms and quenching molecule. Since water vapor shows little quenching action, it can be classed with the weakly quenching gases listed by Norrish and Smith.⁸

Discussions of previous quenching experiments on sodium and other atoms can be found in the books by Mitchell and Zemansky,²¹ and Pringsheim.²²

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²¹ A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation* and *Excited Atoms* (Cambridge University Press, Cambridge, England, 1934), first edition, p. 204.

²² P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949), p. 108.