

## Experimental Evidence for the Absence of Quenching of Sodium Resonance Radiation by Inert Gases\*

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An upper limit of  $10^{-2} \text{ \AA}^2$  is obtained for the quenching cross section of sodium resonance fluorescence when the excited sodium atoms are in collision with inert-gas atoms in their ground state. Excitation of sodium vapor at a pressure of  $5 \times 10^{-7}$  Torr is followed by observation of the decay of the fluorescence using the method of delayed coincidences. The decay time of the fluorescence is unaffected by the presence of the inert gases He, Ne, A, Kr, and Xe at pressures up to 800 Torr, and at temperatures of 130 and 210°C.

THE widespread use of inert gases as buffers in optical pumping and similar experiments has been paralleled by some interest in interactions between alkali-metal atoms in their resonance states and ground-state inert-gas atoms.<sup>1</sup> In particular, the question of whether inert-gas atmospheres could quench alkali resonance radiation has recently been the subject of various speculations. If such quenching were possible, collisions between inert-gas atoms and excited alkali atoms would lead to a complete conversion of the atomic excitation energy into kinetic energy of relative motion and to a consequent decrease in fluorescent intensity, which would be proportional to the inert-gas pressure. Such effects were reported by Nikitin and Bykhovskii<sup>2</sup> and by Chapman and Krause.<sup>3</sup> Quenching collisions, because they induce nonradiative decay of the resonance state, would also make the observed average lifetime of the alkali resonance state in alkali-vapor-inert-gas mixtures shorter than in the pure vapor at low densities. Such a decrease in the lifetime of the  $3^2P$  state in sodium was observed by Demtröder,<sup>4</sup> and it amounted to about 20% at a helium pressure of 300 Torr, corresponding to a quenching cross section of  $0.34 \text{ \AA}^2$ . On the other hand, a recent theoretical investigation by Stamper<sup>5</sup> showed such quenching processes to be impossible.

In order to obtain further experimental evidence for the presence or absence of quenching collisions in sodium-inert-gas mixtures, recently developed methods for precise measurement of atomic lifetimes<sup>6</sup> and of quenching cross sections<sup>7</sup> were applied in a series of lifetime determinations, using sodium vapor in mixtures with helium, neon, argon, krypton, and xenon. Reso-

nance fluorescence was excited by nsec pulses of  $\text{Na}_D$  radiation and the lifetimes were obtained using the technique of delayed coincidences.<sup>6</sup> The procedure for the handling and purification of the inert gases has been described in Ref. 7.

The sodium vapor was maintained in the fluorescence cell at a pressure of  $5 \times 10^{-7}$  Torr by regulating the temperature of the side arm which contained a drop of liquid sodium. It has been shown that, at this pressure, the effects of radiation trapping are negligible.<sup>6</sup> The temperature of the cell could be maintained at up to 100°C above that of the side arm (116°C) permitting the temperature dependence of the quenching collisions to be studied over a limited temperature range.

The observed decay rate, which is equal to the sum of the rates for spontaneous and collisional (quenching) decays, may be represented as follows:

$$1/\tau' = 1/\tau + NQv_r, \quad (1)$$

where  $\tau'$  and  $\tau$  are the observed and natural average lifetimes ( $\tau = 16.3 \text{ nsec}$ ),<sup>6</sup>  $N$  is the atomic density of the

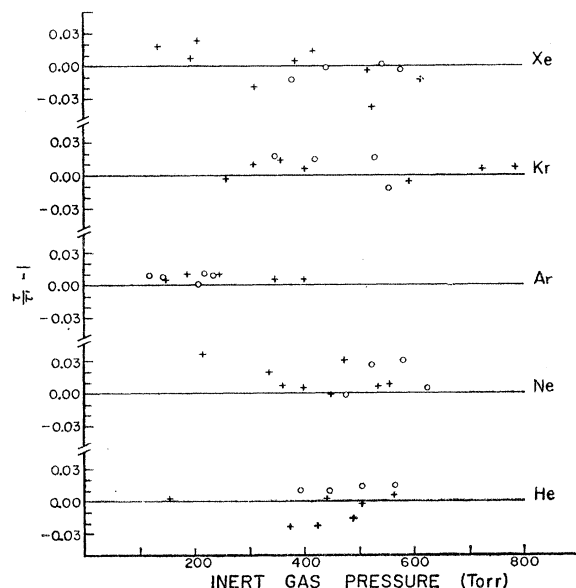


FIG. 1. The variations of  $(\tau/\tau' - 1)$  with pressures of He, Ne, Ar, Kr, and Xe +,  $\tau'$  measured at 130°C; o,  $\tau'$  measured at 210°C.

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<sup>1</sup> L. Krause, *Appl. Opt.* **5**, 1375 (1966).

<sup>2</sup> E. E. Nikitin and V. K. Bykhovskii, *Opt. i Spektroskopia* **17**, 815 (1965) [English transl.: *Opt. Spectry.* (U.S.S.R.) **17**, 444 (1965)].

<sup>3</sup> G. D. Chapman and L. Krause, *Can. J. Phys.* **44**, 753 (1966).

<sup>4</sup> W. Demtröder, *Z. Physik* **166**, 42 (1962).

<sup>5</sup> J. H. Stamper, *J. Chem. Phys.* **43**, 759 (1965).

<sup>6</sup> B. P. Kibble, G. Copley, and L. Krause, *Phys. Rev.* **153**, 9 (1967).

<sup>7</sup> B. P. Kibble, G. Copley, and L. Krause, *Phys. Rev.* (to be published).

quenching gas,  $Q$  is the effective quenching cross section, and  $v$ , is the average relative velocity of the colliding partners. Thus a plot of  $(\tau/\tau' - 1)$  against  $N$  should be linear and its slope should yield  $Q$ , the quenching cross section.

The effective lifetimes were measured at several pressures of each inert gas. The values  $\tau'$  were obtained as averages of three determinations at each inert-gas pressure, which were interspersed with repeated determinations of  $\tau$  in pure sodium vapor. It should be noted that, when inert gas was admitted to the cell, a large decrease in fluorescent intensity was observed, sometimes amounting to 30%. This effect, which was attributed to pressure broadening of the sodium resonance lines, to the presence of very small traces of chemically active impurities in the gases and to local changes in the sodium vapor density, illustrates the inherent unreliability of quenching cross-section determinations from simple intensity measurements.

The experimental results are presented in Fig. 1. It may be seen that, although there is some statistical scatter among the determinations for each gas, there

is no obvious effect of gas pressure on the decay rates, which would manifest itself as a positive slope in the graphs. In each case the points are contained within the limits of  $\pm 0.03$  which correspond to an error, largely statistical in nature, of  $\pm 3\%$  in the determinations of lifetimes by this method. Least-squares analyses of the data led to a maximal value of  $10^{-2} \text{ \AA}^2$  for the quenching cross sections, which should be compared with a high-temperature cross section of the order of  $10^{-3} \text{ \AA}^2$ , suggested by Tsuchiya and Kuratani.<sup>8</sup>

The results of this investigation, which indicate the absence of quenching collisions between sodium and inert-gas atoms, are in disagreement with the experimental data quoted by Nikitin and Bykhovskii<sup>2</sup> and by Demtröder.<sup>4</sup> Their results were, however, obtained under somewhat different experimental conditions without special precautions to eliminate effects due to the trapping of sodium resonance radiation. Imprisonment of radiation, if present, complicates the radiative and collisional processes and makes experimental results difficult to interpret.

<sup>8</sup> S. Tsuchiya and K. Kuratani, *Combust. Flame* **8**, 299 (1964).

## Hartree-Fock Wave Functions for Xe III ( $5p^4, ^3P$ )

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Solutions of the Hartree-Fock equations for the ground-state configuration of  $\text{Xe}^{++}$  have been obtained and tabulated. The corresponding values for the screening parameters, the one-electron eigenvalues, the mean radius, and the mean-square radius are also given.

### 1. INTRODUCTION

THE interest in knowing various properties of inert gases has led the author to calculate atomic wave functions for the ground-state configuration of doubly ionized xenon.

Since the Schrödinger equation cannot be exactly integrated for many-electron atoms and ions, approximate wave functions are calculated in the Hartree-Fock (HF) approximation,<sup>1</sup> because the HF functions are generally accepted as the best one-electron representation of atomic configurations.

In Sec. 2 HF equations and their numerical solutions are briefly discussed. In Sec. 3 radial wave functions, energy eigenvalues, and other quantities related to wave functions are given.

### 2. HARTREE-FOCK EQUATIONS

#### A. General Formulation

The atomic radial wave functions  $P_\alpha(r)$  for atoms or ions with  $m$  shells in the HF approximation are solutions of the set of  $m$  differential equations

$$d^2 P_\alpha(r)/dr^2 + g_\alpha(r)P_\alpha(r) = f_\alpha(r) + \sum_{\nu}^l \epsilon_{\alpha\nu} P_\nu(r), \quad (\alpha, \nu = 1, 2, \dots, m). \quad (1)$$

$\sum_{\nu}^l$  in Eq. (1) means summation over  $\nu$  shells for which  $l_\nu = l_\alpha$ . Each  $P_\alpha(r)$  function is associated with the electrons of the shells of principal quantum number  $n$  and orbital-angular-momentum quantum number  $l$ , and must be normalized and orthogonal to all other wave functions with the same  $l$  value:

$$\int_0^\infty [P_\alpha(r)]^2 dr = 1, \\ \int_0^\infty P_\alpha(r)P_\nu(r) dr = \delta_{\alpha\nu}, \quad (l_\alpha = l_\nu).$$

<sup>1</sup> D. R. Hartree, in *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1955).