

## Inelastic Collisions between Excited Alkali Atoms and Molecules. II. The Quenching of Sodium Resonance Radiation by $N_2$ , $H_2$ , $HD$ , and $D_2$ <sup>†</sup>

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The cross sections for quenching collisions between excited sodium atoms and  $N_2$ ,  $H_2$ ,  $HD$ , and  $D_2$  molecules in their electronic ground states have been determined using a delayed-coincidence method. The sodium atoms in mixtures with the gases were excited with 20-nsec pulses of NaD radiation, and the delays between the exciting and fluorescent pulses were measured with a time-to-pulse-height converter. The resulting pulse-height spectra, which were accumulated in a 400-channel kicksorter, yielded the effective lifetimes  $\tau'$  of the sodium resonance state, which are shorter than the natural lifetime  $\tau$  because of the nonradiative decay induced in collisions with the molecules. The cross sections for collisions with  $N_2$ ,  $H_2$ ,  $HD$ , and  $D_2$ , obtained from an analysis of the dependence of  $\tau'$  on the gas pressures, are  $30.4 \pm 1.2$ ,  $16.2 \pm 0.3$ ,  $11.6 \pm 0.4$ , and  $9.8 \pm 0.3 \text{ \AA}^2$ , respectively.

### I. INTRODUCTION

WHEN sodium vapor at low pressure is illuminated with NaD radiation, the atoms become excited and, in decaying, emit resonance fluorescence which may be observed at right angles to the direction of the exciting light beam. The addition of a molecular gas such as nitrogen or hydrogen to the vapor causes a significant decrease in the fluorescent intensity, which is proportional to the gas pressure. This effect is known as quenching of resonance radiation<sup>1</sup> and is due to inelastic collisions (collisions of the second kind) between the excited sodium atoms and the molecules, in the course of which the atomic excitation energy is converted to translational, vibrational, and rotational energy. Quenching competes with the process of radiative decay and, in nonradiatively transferring excited atoms to the ground state, decreases the observed lifetime. Studies of quenching yield cross sections for the inelastic atom-molecule collisions which, in turn, lead to a better understanding of the collisional interaction mechanisms involved. Most of the earlier experiments involving quenching of atomic resonance radiation have been summarized by Pringsheim.<sup>1</sup> The quenching of alkali resonance radiation has been investigated by Norrish and co-workers<sup>2</sup> and more recently, by Hulpke, Paul, and Paul,<sup>3</sup> and by McGillis and Krause.<sup>4</sup> In most of these investigations, the quenching cross sections were obtained by comparing the intensity of the resonance fluorescence originating from the vapor-gas mixture with that emitted by the pure vapor. The results obtained in this way are extremely sensitive to various extraneous factors which

cause experimental errors that are difficult to estimate or eliminate. It is necessary to maintain the sodium vapor at pressures below  $10^{-6}$  Torr (or  $10^{10}$  atoms/cm<sup>3</sup>)<sup>5</sup> in order to avoid imprisonment of resonance radiation which would further complicate matters. At such vapor densities even a few parts per million of oxygen or other chemically reactive impurity in the quenching gas will react with the sodium vapor, reduce its density in the fluorescence cell and cause a greater decrease in the fluorescent intensity than would result from quenching collisions alone. If, also, the light source<sup>6</sup> used for exciting fluorescence emits NaD lines of half-widths comparable to the absorption half-widths in the pure vapor, additions of quenching gases will cause broadening of the absorption lines, reduce the efficiency of excitation and further decrease the fluorescent intensity.

In the present investigation the effective average lifetimes of the  $3^2P$  states in sodium have been directly determined in relation to the quenching gas pressure, using the previously described technique of pulsed optical excitation.<sup>5</sup> The experimental observations involve only single excited sodium atoms and the results are affected neither by chemical reactions with ground-state atoms nor by pressure broadening, both of which merely cause variations in the number of the excited atoms.

The total observed decay rate is equal to the sum of the decay rates arising from spontaneous emission and from quenching:

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

where  $\tau'$  is the observed mean lifetime in the presence of the quenching gas,  $\tau$  is the natural lifetime,  $N$  is the molecular density of the quenching gas,  $Q$  is the total effective quenching cross section, and  $v_r$  is the average relative velocity of the colliding partners. If the natural lifetime  $\tau$  is known,<sup>5</sup> the quenching cross section may be

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<sup>1</sup> P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949).

<sup>2</sup> See, for example, G. W. Norrish and W. M. Smith, Proc. Roy. Soc. (London) **A176**, 295 (1940).

<sup>3</sup> E. Hulpke, E. Paul, and W. Paul, Z. Physik **177**, 257 (1964).

<sup>4</sup> D. A. McGillis and L. Krause, Phys. Rev. **153**, 44 (1967).

<sup>5</sup> B. P. Kibble, G. Copley, and L. Krause, Phys. Rev. **153**, 9 (1967).

<sup>6</sup> R. J. Atkinson, G. D. Chapman, and L. Krause, J. Opt. Soc. Am. **55**, 1269 (1965).

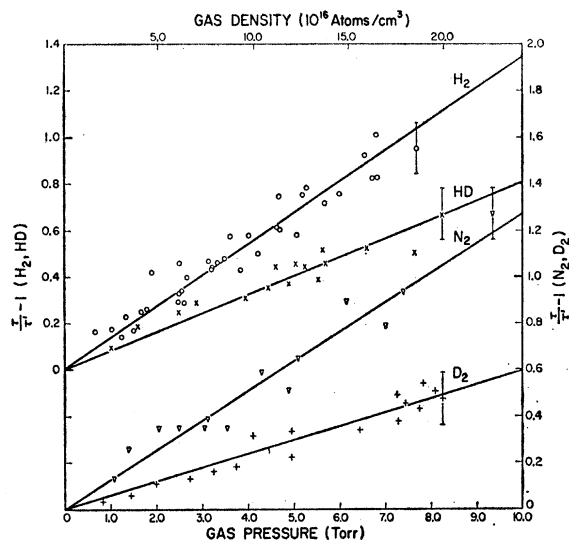


FIG. 1. Quenching of NaD fluorescence by  $N_2$ ,  $H_2$ , HD, and  $D_2$ . The error bars represent statistical error which is nearly the same for every point.

directly obtained from a determination of  $\tau'$  for a range of quenching gas densities.

## II. EXPERIMENTAL

The apparatus used for lifetime measurements has been described elsewhere.<sup>5</sup> Sodium resonance radiation from a spectral lamp was pulsed with a Kerr shutter which produced 10-nsec pulses with a repetition rate of 60 pulses per sec. The light pulses were made incident on the vapor-gas mixture contained in the fluorescence cell. The fluorescent light pulses emerging at right angles to the direction of excitation were detected with a liquid-air-cooled photomultiplier and the time intervals between each excitation and decay were measured with a time-to-pulse-height converter whose output was accumulated in a 400-channel kicksorter.

The fluorescence cell in which sodium vapor was maintained at a pressure of about  $5 \times 10^{-7}$  Torr, was connected by a tube of 3 mm bore to a vacuum and gas-filling system. A system of stopcocks was used to admit controlled quantities of quenching gases whose pressures, ranging from 1–9 Torr, were measured with a trapped McLeod gauge.

Even though gases of the highest commercially available purity were used, the few parts per million of oxygen and other chemically active impurities proved quite troublesome at the low sodium vapor pressure and, before admission to the fluorescence cell, the quenching gases were passed through a liquid-air trap and were further purified by being left for several hours in a small glass vessel whose inner walls were coated with metallic sodium or rubidium. The vessel was flamed with a torch causing vigorous vaporization and mixing of the sodium vapor with the gas. It appeared that gettering purified the gases quite well and little

further chemical reaction with the sodium vapor in the fluorescence cell was observed.

The experimental procedure involved a series of lifetime measurements on a range of vapor-gas mixtures at various quenching gas pressures.  $\tau = 1.63 \times 10^{-8}$  sec was assumed<sup>5</sup> and the resulting values of  $(\tau/\tau' - 1)$  were plotted against  $N$ , the molecular density of the quenching gases. A least-squares analysis of the data yielded the appropriate quenching cross section. This procedure was found to be more reliable and accurate than one in which  $\tau$  and  $\tau'$  were determined in a series of alternating measurements to obtain directly the ratio  $\tau/\tau'$ .

## III. RESULTS AND DISCUSSION

The pulse-height spectra obtained with varying pressures of the quenching gases were exponential in character and appeared similar to those obtained with pure sodium vapor.<sup>5</sup> After subtracting the background counts, the results were analyzed with an IBM 1620 computer using a method similar to that of Bennett, Kindlmann, and Mercer.<sup>7</sup> It was not necessary to correct the resulting values of  $\tau'$  for "pileup" in view of the short lifetimes involved.

The quenching of the fluorescence by  $N_2$ ,  $H_2$ , HD, and  $D_2$  is represented in Fig. 1. As expected, the plots of  $(\tau/\tau' - 1)$  against  $N$ , the density of the quenching gases, are linear and pass through the origin. The quenching collision cross sections, which were obtained from the slopes, are compared in Table I with values quoted by other authors. The uncertainties quoted are purely statistical; any systematic errors are expected to be considerably smaller. There is good agreement with the Na- $N_2$  cross section determined by Hulpke, Paul, and Paul,<sup>3</sup> and by Demtröder,<sup>8</sup> who used the phase-shift fluorometry technique. Their method, like that employed here, depends on a measurement of  $\tau'$  and does not involve a knowledge of the absorption line profile. The results of Norrish and Smith, on the other hand, would tend to be affected by slight impurities in the quenching gases and by pressure broadening of the absorption lines. There is, nevertheless,

TABLE I. Collision cross sections for quenching of NaD fluorescence.

Source	Cross section $Q$ ( $\text{\AA}^2$ )			
	Na- $N_2$	Na- $H_2$	Na-HD	Na- $D_2$
This investigation	$40.3 \pm 1.2$	$16.2 \pm 0.3$	$11.6 \pm 0.4$	$9.8 \pm 0.3$
Norrish and Smith (Ref. 2)	45.6	23.2	...	...
Hulpke, Paul, and Paul (Ref. 3)	36.6	...	...	...
Demtröder (Ref. 8)	43	...	...	..

<sup>7</sup> W. R. Bennett, Jr., P. J. Kindlmann, and G. N. Mercer, *Appl. Optics*, Suppl. 2, 34 (1965).

<sup>8</sup> W. Demtröder, *Z. Physik* 166, 42 (1962).

general agreement as to the significantly larger size of the Na-N<sub>2</sub> cross sections, as compared with the Na-H<sub>2</sub> value, which has been attributed to a relatively easy formation of the Na-N<sub>2</sub> transition complex, caused by a potential unsaturation in the N<sub>2</sub> molecules.<sup>2,9</sup> The small differences between the cross sections for H<sub>2</sub>, HD, and D<sub>2</sub> are of some interest for, although these molecules have identical electronic structures, their vibrational levels differ. The work of Karl and Polanyi<sup>9</sup> suggests that, in a collision between an excited atom and a molecule in the  $v=0$  vibrational state, about one-half of the total available atomic excitation and kinetic energy should be available for transfer to the vibrational levels in the case of H<sub>2</sub> and D<sub>2</sub>, and between one-third and two-thirds in the case of HD. The NaD

<sup>9</sup> G. Karl and J. C. Polanyi, *J. Chem. Phys.* **38**, 271 (1963).

levels are at 17 000 cm<sup>-1</sup> and  $kT$  at 127°C provides an additional 277 cm<sup>-1</sup>, making a total of 8650 cm<sup>-1</sup> available for vibrational excitation in collisions with H<sub>2</sub> and D<sub>2</sub>. This should be compared with the energy interval of 8070 cm<sup>-1</sup> between the most highly populated rotational levels of the ground vibrational state  $v=0$  and the  $v=2$  state in H<sub>2</sub>. The appropriate figures for D<sub>2</sub> are 5860 cm<sup>-1</sup> for excitation of the  $v=2$  state and 8620 cm<sup>-1</sup> for the  $v=3$  state. In HD, either the  $v=2$  or the  $v=3$  states at 7070 cm<sup>-1</sup> and 10 350 cm<sup>-1</sup>, respectively, might be excited. If the lower vibrational states were excited preferentially, the resonance would be closest in the case of H<sub>2</sub>, while a smaller effect would be expected with D<sub>2</sub>. It is doubtful whether these considerations can be used to account for the small differences in the cross sections until a considerably larger volume of experimental data becomes available.

## Elastic Scattering of Lithium Ions in Helium and Hydrogen\*

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The cross sections for elastic scattering of 50- to 800-eV Li<sup>+</sup> ions in He and in H<sub>2</sub> have been measured using a method in which the energy-loss spectrum of the ions is observed as a function of the scattering path length. The experimental procedure yields directly the cross section for scattering outside a given angle which ranges from 10° to 160° in the center-of-mass system. From these data, the interaction potential was computed by a process which involves the numerical integration of the inverted orbit equation for a series of constant angular momenta. The potential so found may be represented by the Born-Mayer form within a few percent as  $V(r) = 3.7 \times 10^2 e^{-5.1r}$  eV for Li<sup>+</sup>-He and  $3.0 \times 10^2 e^{-11.0r}$  eV for Li<sup>+</sup>-H<sub>2</sub>, with  $r$  in Å. The  $V(r)$  for Li<sup>+</sup>-He has also been calculated using the two-center Thomas-Fermi-Dirac statistical model, yielding reasonably good agreement with the experimental result.

### I. INTRODUCTION

THE elastic scattering of one particle by another provides the most direct experimental means of determining the interaction potential energy of the two particles. If, in particular, there is reason to believe that the force is a monotonic function of the internuclear separation, then the scattering can be interpreted unambiguously in terms of a force function.<sup>1</sup> Of particular interest, because of the simplicity of the electron configuration, is the scattering of He by He, or by systems of like configuration. A considerable amount of work has already been done experimentally by Amdur *et al.*<sup>2</sup> and theoretically by Phillipson, Ransil,

Slater and others<sup>3</sup> on the determination of the interatomic potential for He-He. There exists, however, a fairly large discrepancy between experiment and theory for internuclear distances less than about 1.0 Å.

The scattering of Li<sup>+</sup> in He as an experimental problem is much easier than He in He, for, the scattered ion is more readily detected and its energy thus measured. Since, in this case, the incident particle is heavier than the target atom, the angular distribution of the scattered ions will fold back on itself in the laboratory system; that is, for a given laboratory angle of scattering less than the maximum, there will be ions of two energies. Consequently, if an angular distribution is desired, either an energy distribution may be measured directly or the ions that are scattered at a given angle may be energy-analyzed. The energy retained by the ion is, however, a monotonic function of the angle of scattering in the center-of-mass system.

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<sup>2</sup> I. Amdur, *J. Chem. Phys.* **17**, 844 (1949); I. Amdur and A. L. Harkness *ibid.* **22**, 664 (1954); I. Amdur, J. E. Jordan, and S. O. Colgate, *ibid.* **34**, 1525 (1961).

<sup>3</sup> P. E. Phillipson, *Phys. Rev.* **125**, 1981 (1962); B. J. Ransil, *J. Chem. Phys.* **34**, 2109 (1961); J. C. Slater, *Phys. Rev.* **32**, 349 (1928); P. Rosen, *J. Chem. Phys.* **18**, 1182 (1950).