

THE TEMPERATURE DEPENDENCE OF THE QUENCHING OF Na-D-DOUBLET BY N₂ AND H₂O IN FLAMES OF 1500–2500 K

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Abstract—The temperature dependence of the quenching cross section of the Na-D-doublet by N₂ and H₂O molecules has been measured in flames at temperatures from 1500 to 2500 K. The nitrogen and water cross sections are temperature independent. Their values were found to be $\sigma_{\text{N}_2} = (22 \pm 2) \text{ \AA}^2$ and $\sigma_{\text{H}_2\text{O}} = (2.2 \pm 0.3) \text{ \AA}^2$. Our value of the nitrogen cross section is about half of the value measured at about 400 K in vapour bulbs. A possible explanation for this difference is given.

1. INTRODUCTION

MOST of the experiments done on quenching and excitation of alkali atoms have been performed at temperatures of about 400–600 K with various techniques.^(1–4,7) Some experiments have been done in flames at temperatures from about 1400 to 2000 K.^(5,6) Quenching has also been studied in shock-heated gases at temperatures of 2500–3000 K.^(8,29) For Na-quenching by N₂, the cross sections measured at different temperatures differ by about a factor 2. It is not certain whether this difference is due to a systematic temperature dependence of the cross section or to experimental errors.

Recently, some theoretical studies have been reported on Na–N₂ quenching in which, however, some serious approximations have been made. Using the Landau–Zener method of curve crossing, BJERRE and NIKITIN⁽⁹⁾ and BAUER *et al.*⁽¹⁰⁾ have calculated theoretically the cross section for this quenching process. The order of magnitude of their calculations agreed well with the experimental results. The theory predicts also the occupation distribution of the vibrational levels of the diatomic molecule after quenching has taken place. BAUER *et al.* also predict that the cross section should be independent of the relative velocity of the collision partners, in an energy range of 0.04–0.5 eV. The validity of their theory may thus be checked by measuring the temperature dependence of this cross section. However, the interpretation of the temperature dependence of cross sections measured in flames and vapour bulbs is complicated by the fact that the measured cross sections are averaged over the Maxwell distribution of the relative velocities, as well as over the Boltzmann distribution of the initial vibrational states of the molecule. An interesting experiment that escapes this difficulty has been described by BRUS,⁽¹¹⁾ who has measured the quenching of Na by I₂ by using the method of photodissociation of NaI. These measurements yield directly the cross section as a function of relative velocity, which is controlled by the wave length of the radiation used for the photodissociation, independently of the initial

vibrational energy distribution of the molecule. A crossed molecular beam method has recently been applied, by MENTALL *et al.*⁽¹³⁾ and KALFF,⁽¹²⁾ to study the excitation process of Na by a hot nitrogen beam. The advantage of this method is that the distribution of vibrational and translational energies can be varied independently within certain limits. The excitation rate constant can be related to the quenching rate constant by the principle of detailed balance. So the results of excitation and quenching experiments can be compared.

In view of the possible velocity dependence of the quenching cross section and of the existing differences in the values measured under different conditions at different temperatures, it seemed useful to establish more systematically and precisely the temperature dependence of the quenching cross section of Na by N₂ and other species. To that end, flames were used over a reasonably wide temperature range of 1000 K.

2. EXPERIMENTAL METHOD

In flames, the quenching cross sections are deduced from the fluorescence yield factor, which is defined as the fractional probability that an excited atom loses its energy by radiation of a photon.

A metal salt solution is sprayed into the flame, which is irradiated by a light-source that excites the metal atoms to the considered states. The fluorescence yield is derived from the measured ratio of the absorbed and re-emitted amount of energy.

The fluorescence yield factor can be theoretically expressed in the rate constants for radiative and collisional de-activation of the excitation level concerned. However, complications arise when the line has a fine structure. In our case we measured the absorption as well as the re-emission of both the Na 3²P doublet lines together. According to JENKINS,⁽¹⁴⁾ the yield factor *Y* is then given by

$$Y = \frac{1}{1+\gamma} \left\{ \frac{\gamma \{ A_{20}(A_{10}+k_{10}+k_{12}) + A_{10}k_{21} \} + A_{10}(A_{20}+k_{20}+k_{21}) + A_{20}k_{12}}{(A_{10}+k_{10})(A_{20}+k_{20}+k_{21}) + k_{12}(A_{20}+k_{20})} \right\}. \quad (1)$$

Denoting the ground state ²S_{1/2} by the number 0, the ²P_{1/2} state by 1 and the ²P_{2/3} state by 2, we have *A*_{*ij*} = transition probability for spontaneous emission from state *i* to state 0, *k*_{*ij*} = collisional rate constant, defined as the number of collisions per atom per second, leading to the transfer of atoms from the state *i* to the state *j*; *γ* is defined as the ratio of the absorbed amount of energy by transitions into the ²P_{3/2} state and the absorbed amount of energy by transitions into the ²P_{1/2} state. The value of *γ* depends on the ratio of the oscillator strengths of the two lines, the concentration of metal atoms in the flame and the spectral-intensity distribution of the primary light-source. In the case of the sodium doublet, equation (1) can be simplified by putting *A*₁₀ = *A*₂₀, which introduces an error of less than 1 per cent.

As far as we know, no experiments have been done on the quenching of sodium with separated doublet lines. However, there are experiments of this kind on the quenching of potassium, rubidium and cesium^(15,29) at temperatures of about 400 K which indicate that *k*₁₀ and *k*₂₀ are equal within about 10 per cent for these alkalis quenched by nitrogen. We proved by experiments on the quenching and mixing of Rb by nitrogen and water

molecules that this equality holds within 5 per cent for these partners at flame temperatures.⁽¹⁶⁾ Therefore, we may put $k_{10} = k_{20}$ in the case of sodium because of its much smaller doublet splitting. Then formula 1 reduces to the simple form (see Appendix 2)

$$Y = A/(A + k), \quad (2)$$

with $A = A_{10} = A_{20}$ and $k = k_{10} = k_{20}$. It should be stated, that in the derivation of equation (2) no assumptions concerning k_{21} , k_{12} and γ have to be made. So we are able to deduce unambiguously the collisional de-excitation rate constant k from Y with known values of A .

In a flame containing various types of molecules, the overall rate constant k occurring in equation (2) is a summation of the specific rate constants corresponding to the various kinds of flame particles denoted by j

$$k(T) = \sum_j k_j(T) = \sum_j n_j \bar{g}_j \sigma_j(T), \quad (3)$$

with n_j = density of quenching particles of kind j , \bar{g}_j = mean relative velocity of the alkali atoms and quenching particles of kind j , $\sigma_j(T)$ = effective quenching cross section at temperature T . The meaning of this effective cross section is rather formal and does not allow a simple interpretation. We shall use it only as a convenient way of expressing k . Furthermore, n_j and \bar{g}_j are given by $n_j = p_j/(kT)$, $\bar{g}_j = (8kT/\pi\mu_j)^{1/2}$, with p_j = partial pressure of flame particles of kind j , k = Boltzmann's constant, T = absolute temperature, μ_j = reduced mass of sodium and particle of kind j . The major components in our flames are argon atoms, nitrogen- and water-molecules. Thus

$$p_{N_2} \sigma_{N_2}(T) + p_{H_2O} \left(\frac{\mu_{N_2}}{\mu_{H_2O}} \right)^{1/2} \sigma_{H_2O}(T) + p_{Ar} \left(\frac{\mu_{N_2}}{\mu_{Ar}} \right)^{1/2} \sigma_{Ar}(T) = \left(\frac{\pi \mu_{N_2} k T}{8} \right)^{1/2} A \left(\frac{1}{Y} - 1 \right). \quad (4)$$

In order to derive from our experiments the effective cross sections separately we proceeded as follows. For five different temperature values, we constructed an isothermal set of flames of various compositions. The input gases O₂, H₂, N₂ and Ar were controlled in such a way that each set of flames satisfied the following demands (1) the flames were stoichiometric at constant total pressure of 1 atm; (2) the temperature was the same for all flames in each set within 50 K; (3) the partial water pressure was the same for all flames in each set. These requirements were achieved by replacing part of the N₂ flow by argon. The details of the flame compositions used are shown in Table 1.

Argon is known to have a negligible quenching effect,^(7,8,17,18,23) but the mixing effect of argon is quite noticeable. Because of the fact that we may put $k_{10} = k_{20} = k$, the mixing rate constants drop out of equation (2) and so the mixing does not influence our measurements. The consequence of the constant partial water pressure, within each isothermal set, is that the difference in the Y values measured, within each set, is only related to the different concentration of N₂ molecules, according to

$$p_{N_2} \cdot \sigma_{N_2}(T) + C_1 = C_2 \left(\frac{1}{Y} - 1 \right); \quad (5)$$

C_1 and C_2 are constants for each isothermal series of flames. They depend on the temperature T while C_1 depends also on the water concentration in each isothermal series. Plotting $(1/Y - 1)$ as a function of p_{N_2} , we obtain $\sigma_{N_2}(T)$ from the slope of this graph.

TABLE I

Flame number	Unburnt gas-mixture in l/min				Composition of flame gas (in partial pressures)*					Temperature (K)	Y value
	Ar	N ₂	H ₂	O ₂	Ar	N ₂	H ₂ O	H ₂	O ₂		
1	0	5.0	6.0	3.0	0	0.44	0.50	0.03	0.01	2494	0.076
2	0.79	4.0	5.75	2.87	0.07	0.37	0.50	0.03	0.01	2494	0.087
3	1.58	3.0	5.5	2.75	0.15	0.29	0.50	0.03	0.01	2491	0.102
4	2.37	2.0	5.25	2.63	0.24	0.20	0.50	0.03	0.01	2497	0.134
5	5.0	0	4.5	2.25	0.51	0	0.46†	0.02	0.01	2490	0.36
6	0	5.0	3.65	1.82	0	0.58	0.41	0.01		2220	0.071
7	0.78	4.0	3.5	1.75	0.09	0.48	0.41	0.01		2218	0.084
8	1.59	3.0	3.35	1.67	0.20	0.38	0.41	0.01		2227	0.010
9	2.21	2.0	3.07	1.53	0.30	0.27	0.41	0.01		2250	0.136
10	4.5	0	2.5	1.25	0.63	0	0.36†	0.01		2250	0.45
11	0	5.0	2.38	1.19	0	0.68	0.32			1971	0.053
12	0.81	4.0	2.28	1.14	0.12	0.56	0.32			1963	0.064
13	1.3	3.0	2.05	1.02	0.21	0.47	0.32			1972	0.072
14	1.57	2.0	1.7	0.85	0.30	0.38	0.32			2000	0.092
15	4.5	0	1.5	0.75	0.75	0	0.25†			2000	0.58
16	0	5.0	1.61	0.80	0	0.76	0.24			1738	0.045
17	1.4	4.3	1.61	0.80	0.19	0.59	0.22			1737	0.055
18	2.6	3.7	1.61	0.80	0.33	0.47	0.20			1718	0.066
19	4.0	3.0	1.61	0.80	0.46	0.35	0.19			1710	0.089
20	5.0	0	1.0	0.50	0.83	0	0.17†			1760	0.67
21	0	5.0	1.0	0.50	0	0.83	0.17			1510	0.041
22	1.41	4.0	1.0	0.50	0.22	0.62	0.16			1515	0.053
23	2.6	3.12	1.0	0.50	0.39	0.46	0.15			1490	0.068
24	5.0	0	3.5	1.75	0.58	0	0.38	0.02		2400	0.40
25	4.0	0	2.0	1.0	0.66	0	0.33	0.01		2136	0.51
26	4.0	0	1.0	0.5	0.80	0	0.20			1820	0.63

* Partial pressures smaller than 5×10^{-3} have been omitted.

† When using the results for these flames in our plots, we corrected the partial pressures and thus the k -values in order to make the water contribution in these flames equal to the water contribution in the corresponding flames for each isothermal series.

This procedure has been repeated at five different temperatures, with intervals of about 250 K between them. It should be noted that the quenching cross section for H₂O can be obtained from the intersection of the extrapolated graph with the ordinate axis, which yields

$$\sigma_{\text{H}_2\text{O}}(T) = \frac{1}{p_{\text{H}_2\text{O}}} \left(\frac{\pi \mu_{\text{H}_2\text{O}} \cdot kT}{8} \right)^{1/2} A \left(\frac{1}{Y_0} - 1 \right),$$

where $(1/Y_0)$ is the extrapolated value of $(1/Y)$ for zero nitrogen concentration.

3. EXPERIMENTAL SET-UP

The experimental arrangement is similar to that described in Ref. (19). Here we describe only some improvements that have been made. Because we wanted to extend our measurements to flame temperatures that are as high as possible, we had to improve the signal-to-noise ratio, which was generally rather poor in flames with temperatures exceeding about

2250 K due to the relatively strong thermal emission of the Na-line. This improvement was realized by choosing a modulation frequency of about 1 kHz, which lies closely to the optimal modulation frequency for our flame system.⁽²⁴⁾ The vacuum phototube signal was detected by a lock-in amplifier (P.A.R. model 121) tuned at this frequency and recorded by a Servogor recorder. The flow and metering system was modified so as to make it possible to premix and supply 4 kinds of gases together to the burner. A circular, water cooled Meker burner with 631 holes of 0.5 mm dia. was used. The central flame, coloured by Na-vapour, was surrounded by a mantle flame of approximately the same composition but without metal vapour supply. The metal-salt solution was sprayed into the centre of the flame only by means of a chamber-type nebulizer. The mantle flame, in turn, was surrounded by another mantle of cold argon gas in order to prevent the infusion of air into the flame and to steady the inner flame. The presence of this argon mantle did not noticeably change the *Y*-values measured in the pure-argon cooled flames. So we can safely assume that infusion of N₂ and O₂ from the surrounding air did not affect our measurement. The pure-argon cooled flames, having the highest *Y*-values, are the most sensitive ones for such effects, if they would be present at all.

As a primary radiation source, a Philips highway lamp was used. Although the Na-lines emitted by this lamp are expected to be rather broad and self-absorbed, it appeared that our fluorescence signal was about a factor 5 larger with this lamp than with a normal Philips spectral sodium lamp. Due to the relatively larger linewidth of the former lamp and correspondingly small absorption factor, we had to use zero-suppression in order to measure precisely the absorbed primary radiation in the flame. The long-term drift of our lamp was less than a few percent during several hours. So, no special stabilizing techniques were required.

Our method of measuring the *Y*-values has been fully described in Refs. (19) and (20), but it will be summarized here briefly. At a certain low metal concentration, we measured the amount of absorbed energy by placing the lamp and flame in line with the photodetector. Then the axis connecting the flame and photodetector was turned over 90° and the flux of fluorescence radiation incident on the phototube was measured in the same relative units as the absorbed radiation flux. The fluorescence radiation was assumed to be isotropically re-emitted, which appears to be true when self-absorption is negligible.

The ratio of the fluorescence signal, corrected for the limited solid angle subtended by the optical system and for filter attenuation, to the absorption signal yields the apparent *Y*-value at this particular concentration. However, the *Y*-value thus found is still concentration-dependent due to reabsorption of the fluorescence light on its way out of the flame centre.⁽²⁷⁾ By linear extrapolation to zero concentration in the range of low metal concentration, where the self-absorption loss is low and proportional to concentration,⁽¹⁹⁾ one finds the true *Y*-value.

The flame temperatures were measured by applying the method of line-reversal to the stronger component of the Na-D doublet, using the accurate photo-electric measuring device developed by SNELLEMAN.⁽²⁰⁾ However, because of possible radiative dis-equilibrium in the flame, the line-reversal temperature can deviate from the "true" flame temperature at low Na-concentrations.^(6,19) The latter temperature is assumed to be constant throughout the cross-section of the colored central flame at the height of measurement. We avoided this difficulty by measuring the line-reversal temperature as a function of high metal concentration and extrapolating the result to infinite concentration.

4. MEASUREMENTS AND RESULTS

All data obtained are listed in Table 1.

The following sources of error are critically examined for possible contribution to the uncertainty in the experimental values. In addition to the three major flame components considered above, other species in the flame (such as O_2 , H_2 and free radicals) may have a non-negligible quenching effect. Because of the very low partial pressure of the Na-atoms, ions or compounds in the flame (of the order $1:10^9$), these species will have a negligibly small quenching effect on the excited Na-atoms. We note from Table 1 that all flame components other than nitrogen and argon occur in each isothermal series in practically constant concentrations. The determination of the nitrogen cross section is thus not affected by these components, but they may affect the water cross section. From the flame compositions listed in Table 1, it appears that the other species may have a noticeable effect on the quenching only in the hotter flames ($T > 2000$ K) assuming that these quenching cross sections are not extraordinary large (say $< 500 \text{ \AA}^2$).

The measurement of the Y -value in each flame was repeated at least twice except for the flames at 1500 K which were measured at least five times, as only three isothermal flames were at our disposal at this temperature. Each true Y -value was determined with a least-squares procedure from the plot of apparent Y -values and was measured for a series of about 15 Na-concentrations. The least square error in the true Y -values was in general less than 3 per cent; however, the reproducibility between different series of measurements was, in general, worse (< 10 per cent). According to equation (5), in each isothermal series, the Y -value was plotted against p_{N_2} which was calculated from the equilibrium flame composition. Again using a least-square procedure, we found the nitrogen cross section, σ_{N_2} , from the slope of the straight line. Figure 1 shows an example of such a plot in the hottest flame series. The experimental error in our measurements is fully determined by the instability of the sprayer and by small fluctuations in the gas supplies. A possible

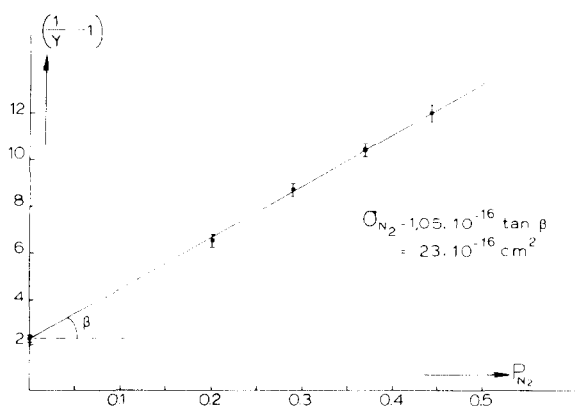


FIG. 1. An example of a plot of the results from the measurements of the fluorescence yield factors Y for the Na-D-doublet in an isothermal series of 5 flames, at temperature $T = 2494$ K. $(1/Y) - 1$ has been plotted as a function of the partial pressure of nitrogen, p_{N_2} . Here p_{N_2} is dimensionless because the conversion factor for atmospheric pressure has been accounted for in the proportionality constant between σ_{N_2} and $\tan \beta$.

calibration error of the flowmeters is expected to be less than 1 per cent. The uncertainty in the reading of the flowmeters can cause an error in the supplied amount of gas of at most 2 per cent. The setting of the flowmeters was continuously checked, so we can expect that an incidental missetting has hardly influenced the final result. Moreover, missettings of the H_2 and O_2 flowmeters were found to have only a noticeable effect on the Y -value measured in pure argon-cooled flames. Because of the negligible argon cross section and the small H_2O cross section, a small increase in oxygen or hydrogen will strongly decrease the Y -value. Using the cross sections for H_2 and O_2 from Ref. (6) we calculated the Y -value to be maximal when the input gas mixture is stoichiometric. Indeed, we measured in the stoichiometric argon cooled flames the highest Y -values. This result proves, indirectly, the correctness of our flow calibration and the negligible effect of calibration errors on the Y -values determined in the other flames. Furthermore, we calculated the influence of the rate of water aspiration (in ml./min) on the flame-gas composition. This rate depended on the flow of vaporizing gas (N_2 or Ar). In the most unfavorable case, i.e. in the coldest flame with the highest nitrogen flow (flame no. 21), the contribution of the sprayed water to the H_2O pressure in the flame was at most 10 per cent. In all other flames, it was less and negligibly small. We found that systematic errors in the temperature measurement, due to radiative disequilibrium, will be no larger than 10 K. The statistical error in the temperature measurements differs from ≈ 2 K in hot flames to ≈ 25 K in cool flames. The actual flame temperatures within each isothermal series of flames agreed within 50 K among each other. From the mutual agreement, within experimental error of 25 K, found for the line-reversal temperature measured with both the Na 3^2P and K 4^2P doublets down to flame temperatures of 1500 K, we conclude that our measurements were not affected by suprathreshold chemiluminescence, which might be found in the coolest flames.^(21,28) The influence of the experimental error in the temperature on the flame-gas composition appeared to be negligible.

The temperature dependence of σ_{N_2} for the quenching of the sodium D-doublet by nitrogen, in the range from 1500 to 2500 K, is shown in Fig. 2. No systematic variation of σ_{N_2} with T is found in this range within the experimental error of about 10 per cent. The

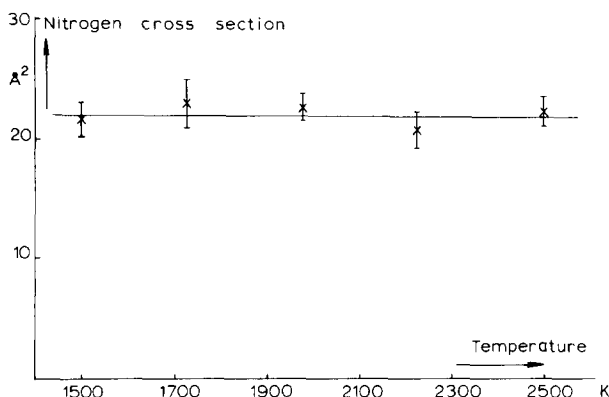


FIG. 2. The temperature dependence of the cross section for the quenching of the Na-D-doublet by nitrogen in the region of 1500–2500 K, as measured in five series of isothermal flames.

mean value of the cross section is $(22 \pm 2) \text{ \AA}^2$ in the entire temperature range measured. The vertical error bars in Fig. 2 are due to statistical spreads in the Y -values found in separate measurements. The experimental error in σ_{N_2} amounts to less than 10 per cent.

We also derived the quenching cross section of the sodium D-doublet by water molecules. Three additional stoichiometric argon-cooled flames (No. 24, 25, 26) were constructed at temperatures between those of the isothermal series. The lowest attainable temperature with pure argon-cooled flames was about 1750 K. This limit was set by blow-off of the flame, whereas the limit on the high temperature side was set by flashback of the flame. As already mentioned, in pure argon cooled flames, we cannot *a priori* neglect the presence of dissociation products in flames with temperatures above 2000 K. Therefore, we calculated $\sigma_{\text{H}_2\text{O}}$ from the Y -value measured in the pure argon-cooled flames of lowest temperature (1750 K). Then we need not make corrections for the effects of the other species. The result is $\sigma_{\text{H}_2\text{O}} = (2.2 \pm 0.3) \text{ \AA}^2$. Assuming $\sigma_{\text{H}_2\text{O}}$ to be temperature-independent, and taking from Ref. (6) $\sigma_{\text{H}_2} = 8 \text{ \AA}^2$ and $\sigma_{\text{O}_2} = 35 \text{ \AA}^2$ and again assuming temperature-independence, we calculated, from the known flame composition, the overall quenching-rate constant in the other hotter six pure argon-cooled flames.

These calculations were compared with the measured rate constants in Fig. 3. From the agreement found, we may conclude that the assumption of a temperature independent $\sigma_{\text{H}_2\text{O}}$ is justified. A consequence of this result is that the quenching cannot proceed by the process $\text{Na}^* + \text{H}_2\text{O} \rightarrow \text{Na} + \text{H} + \text{OH}$ because this reaction requires an activation energy of about 3 eV. This would result in a strongly temperature dependent rate constant. This quenching mechanism has been proposed by ZEEGERS⁽²²⁾ to explain quenching of the $K 5^2P$ doublet measured by HOOYMAYERS.⁽¹⁹⁾

As mentioned, we neglected the O, H and OH contributions in our calculations. As far as O- and H-atoms are concerned, this can be justified because quenching of sodium by single atoms is generally known to be an inefficient process when the electronic excitation levels of the atoms lie relatively far from the $\text{Na } 3^2P$ level. The OH contribution could not be accounted for by lack of data on its quenching effect. An estimate shows, however, that if the quenching cross section for Na by OH is of the same order as the H_2 cross section,

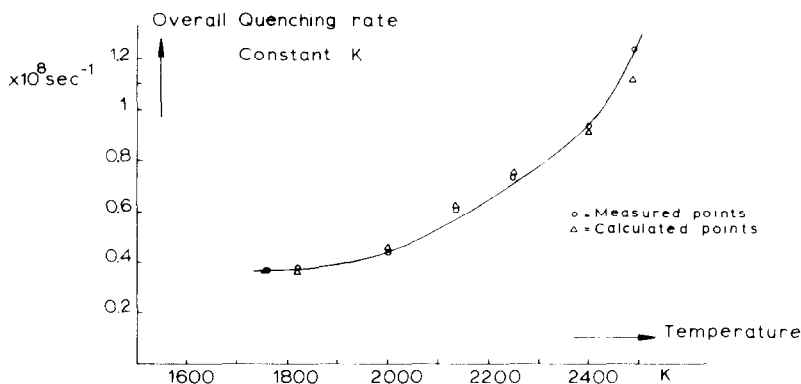


FIG. 3. Measured and calculated overall quenching rate constants k in seven argon-cooled flames of different temperatures. The calculation has been done on the assumption that the quenching cross sections for the different major species in the flames are not temperature dependent.

the contribution of OH is about a factor 7 smaller than that of H₂ and O₂ together in the hottest argon-cooled flame and even smaller in other flames. Furthermore, it appears that our value of $\sigma_{\text{H}_2\text{O}}$, calculated from the argon-cooled flame at 1760 K (containing no N₂), agreed within 10 per cent with the value obtained from the nitrogen-cooled flames at 1500 K by extrapolation to zero N₂-pressure. Hence we conclude that the H₂O cross section is temperature-independent within about 15 per cent in the temperature range from 1500 to 2500 K.

5. DISCUSSION

In Fig. 4, we plotted all available Na–N₂ quenching cross sections measured in the last years, in bulk systems, where a temperature can be meaningfully defined. We should mention that the vapor bulb experiments at 400–600 K have been done using several techniques^(1–4) so that significant systematic errors in these results are not likely to be present. The results of the flame experiments⁽⁵⁾ for σ_{N_2} and $\sigma_{\text{H}_2\text{O}}$ agree within experimental error (our error range for $\sigma_{\text{H}_2\text{O}}$ lies within the error range reported by Jenkins and conversely for σ_{N_2}). Neither Jenkins nor we found evidence for a temperature dependence of σ_{N_2} and $\sigma_{\text{H}_2\text{O}}$ in the temperature region of 1500–1800 K. BÄSTLEIN'S⁽⁷⁾ results lie between these two groups of data. He made measurements at two different temperatures around 600 K and has found some evidence for a temperature-dependent cross section. The results of Tsuchiya, who has measured line reversal temperatures in shock tubes at temperatures around 3000 K, are too inaccurate for use in establishing the temperature dependence. He has reported recently the N₂ quenching cross section to be of the order of 30 Å^2 ,^(8,26) so this value will not be considered further.

As far as we know there are only two more recent experiments where the velocity dependence of a quenching cross section has been explicitly studied. GATZKE⁽²⁵⁾ has

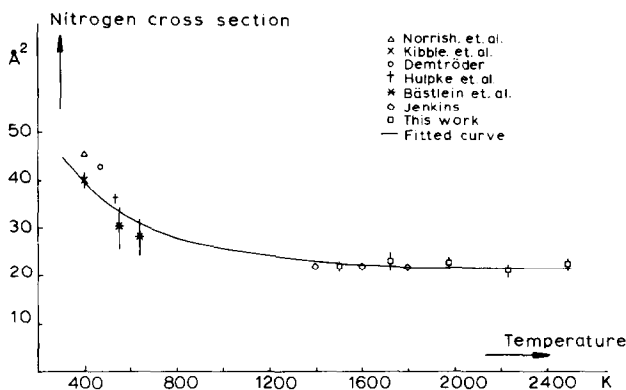


FIG. 4. A survey of measured cross sections for the sodium D-doublet, quenched by nitrogen, as a function of temperature. The curve has been fitted to the experimental points as described in Appendix 1.

measured the quenching of the K 4^2P doublet by N_2 and CO_2 using the method of photodissociation of KI in vapour bulbs. He has reported a decrease of the quenching cross section with increasing relative velocity g . The velocity dependence was about proportional to g^{-1} for CO_2 but less for N_2 . As already mentioned, BRUS⁽¹¹⁾ has measured the velocity dependence of the cross section of quenching of Na 3^2P by I_2 with the same method of photodissociation. He has also reported a decreasing cross section with increasing relative velocity. It should be noted that the magnitudes of relative velocities studied in these experiments are of the same order as in our experiment.

We have tried to explain the combined literature data in Fig. 4 for the Na- N_2 quenching cross section. In fact, a temperature dependence for the effective cross section may be caused by the combined result of averaging over the Maxwell velocity distribution of a cross section which depends on the relative velocity and the effect of the Boltzmann distribution of the initial vibrational states. First we consider only a velocity-dependent cross section and neglect a possible influence of the vibrational distribution. Then taking $\sigma = a \cdot (1/g^q)$ as a trial function (with $a = \text{constant}$), it can be shown that in order to explain the experimental behaviour, q must have about the value 3 or greater in the low velocity region ($g < 10^5$ cm/sec), while q should be practically zero in the high velocity region ($g > 10^5$ cm/sec). The velocity dependence can only play a part at low velocities otherwise the effective cross section would not be constant in the measured flame temperature range. But this implies also that the velocity dependence in this low velocity range should be rather strong. These conclusions are based on considerable overlap of the Maxwellian velocity distributions at 650 and 1400 K.

A second possibility is that the Boltzmann distribution over the initial vibrational states of the nitrogen molecule introduces an extra apparent temperature dependence if σ is different for different initial vibrational levels. The population of vibrational states higher than the vibrational ground state cannot be neglected at flame temperatures. It should be mentioned here that the results of Gatzke and Brus are not affected by this effect. We tried to explain the available experimental data, using the same trial function for the velocity dependence of the cross-section and assuming dependence of σ on the initial vibrational state. The dependence of the cross section on the initial vibrational state, n , is obtained from a best fit to the experimental points. The details are shown in Appendix 1. We obtained a reasonable fit by assuming a velocity dependence proportional to g^{-1} in the entire g -range and assuming that the cross section for quenching transitions, starting from vibrational levels $n = 1, 2$, are, respectively, about a factor 2 and 3 larger than the cross section for transitions starting from level $n = 0$. Of course, the uncertainty in these ratios is large, especially for the larger n value (see Appendix).

Although an increase of cross section for vibrationally-excited nitrogen seems to be possible, since the crossing region of the potential energy curves shifts to larger intermolecular distances, such a strong influence would not be expected. More experimental data are required for an unambiguous interpretation of the dependence of σ on T that is suggested by Fig. 4. Especially, additional quenching results in the region of 600–1400 K, together with excitation results measured in a velocity selected molecular beam experiment, would be very welcome.

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APPENDIX 1

Interpretation of the observed temperature dependence of the quenching cross section of Na by nitrogen

Taking into account all possible vibrational transitions in the quenching collision, the overall rate constant may be written as

$$k_{qu}(T) = \sum_{n,n'} e^{-E_n/KT} \frac{1}{Q(T)} \int_{E_{n,n'}}^{\infty} \sigma_{qu}(E, n, n') \cdot \left(\frac{2E}{\mu}\right)^{1/2} f(E) d(E). \quad (6)$$

Here E = relative kinetic energy before the quenching, $f(E)$ = Maxwell distribution of relative kinetic energy, $Q(T)$ = vibrational partition function of the diatomic molecule, E_n = energy of n th vibrational level with respect to the vibrational ground state, $\sigma_{qu}(E, n, n')$ = quenching cross section as a function of E for a given vibrational transition from n to n' , $E_{n,n'}$ = the lower integration limit given by the relation $E_{n,n'} = (E_{n'} - E_n - E_{ex})$

if $(E_{n'} - E_n) \geq E_{ex}$ and $E_{n,n'} = 0$ otherwise, E_{ex} = the excitation energy of Na. For simplicity, we have neglected the contributions of the rotational energy. It is difficult to assess its role in the quenching process because of lack of further information.

It is clear from equation (6) that the concept of an effective cross section, as introduced in equation (3), has no simple physical meaning in a situation in which several reaction channels are possible. We note that the mean relative velocity, by which the overall rate constant should be divided, is not always uniquely defined when there are several reaction channels opened for which the lower integration limit of E differs from zero. Because the lower integration limit for each channel depends on E_n , the Boltzmann factor also complicates a physically meaningful definition of an effective quenching cross section. However, if we neglect the contribution of the channels for which $E_{n,n'} \neq 0$, we can define an effective cross section in the usual way (see equation 3). This neglect seems to be justified because the condition $E_{n,n'} \neq 0$, would imply that, apart from all of the excitation energy of the sodium atom going into vibrational energy, an additional amount of translational energy is transferred into vibrational energy during the quenching collision.

Available data^(30,31) on the state of vibrational excitation after quenching of metal atoms by molecules point to $E_{n'} < E_{ex}$ and, therefore $E_{n'} - E_n < E_{ex}$. So we can expect that the relative contribution of these transitions to the overall rate constant is rather small, although one should be careful by extrapolating the results obtained for quenching of Hg to quenching of alkali metals.

We shall take the simple trial function

$$\sigma_{qu}(E, n, n') = a(n, n') \cdot E^p, \quad (7)$$

where p is a constant in the E -range considered by us. Then, from equation (6),

$$(\sigma_{qu}(T))_{\text{eff}} = \frac{k_{qu}(T)}{\bar{g}} = \sum_n \frac{e^{-E_n/kT}}{Q(T)} \cdot (kT)^p \cdot \Gamma(p+2) \cdot a(n), \quad (8)$$

where $\Gamma(p+2)$ is the normal gamma function and

$$a(n) \equiv \sum_{n'} a(n, n'). \quad (9)$$

Equation (9) has been introduced because the summation over n' in equation (6) influences the temperature dependence of the rate constant only indirectly and our quenching experiment can give no information about n' . Now we put $a(n) = a_n \cdot a(0)$, where a_n is a constant which depends only on n and $a(0)$ is a constant which is determined by fitting the calculated temperature dependence of equation (10) to the measured temperature dependence. Equation (3) reduces then to

$$(\sigma_{qu}(T))_{\text{eff}} = a(0) \sum_n \frac{e^{-E_n/kT}}{Q(T)} \cdot (kT)^p \cdot \Gamma(p+2) \cdot a_n. \quad (10)$$

We have tried to fit equation (10) to the experimental quenching data shown in Fig. 4 as a function of T . A reasonable fit is obtained if $p = -0.5 \pm 0.25$, $a_0 = 1$, $a_1 = 2 \pm 0.5$, $a_2 = 3 \pm 1.5$, and $a(0) = 1.1 \times 10^{-21} \text{ cm}^2 \text{ erg}^{1/2}$. Only the states with $n = 0, 1, 2$ are important in the case of the Na-doublet quenched by N_2 up to temperatures of 2500 K; $a(0)$ is a proportionality constant which is fixed by a particular choice of p and of the a_n .

Thus the Na quenching cross section appears to increase with increasing vibrational number (up to 2) of the initial vibrational state of N₂.

APPENDIX 2

Effect of ground state depletion in a.c. fluorescence measurements

In this appendix, we shall derive an expression for the fluorescence yield factor as measured by the a.c. modulation method, taking into account the depletion of ground-state atoms by the photo-excitation process.

The sodium atoms in the flame are irradiated by a modulated light beam. For the sake of simplicity the atom is assumed to have only a ²S ground state and one excited state with weight factor 6. For convenience, the on-off switching of the beam is supposed to be instantaneous. The modulation frequency ($\approx 10^3$ Hz) is low enough in comparison with the transition probability of the sodium 3²P level ($\approx 10^8$ Hz) in order to assure that a steady-state situation is reached within half the modulation period. We can now write two steady-state equations, namely:

(a) with the beam on,

$$q(n_0 + \Delta n_0) + k_{01}(n_0 + \Delta n_0) = k_{10}(n_1 + \Delta n_1) + A(n_1 + \Delta n_1); \quad (11)$$

(b) with the beam off,

$$k_{01}n_0 = (k_{10} + A)n_1; \quad (12)$$

where q = probability per sec per Na atom for photo-excitation by the external light beam, k_{01} = probability per sec per Na atom for collisional excitation, k_{10} = probability per sec per Na atom for collisional de-excitation, A = probability per sec per Na atom for de-excitation by light-emission, n_0 = ground state Na-atom concentration, n_1 = excited state Na atom concentration, Δn_0 = change in ground-state atom concentration due to the external light beam, Δn_1 = change in excited state atom concentration due to the external light beam. We have assumed that the influence of the thermal radiation field present in the flame can be neglected. This can be justified because we measure fluorescence yield factors only at low metal concentrations and extrapolate to zero concentration. The same assumption implies, of course, that reabsorption of the fluorescence light can be neglected. Also stimulated emission can be neglected. Because the total number of atoms per cm³ is constant, it follows that

$$\Delta n_0 = -\Delta n_1. \quad (13)$$

By subtracting equations (11) and (12) and using equation (13), we get

$$\Delta n_1 = \frac{q(n_0 + \Delta n_0)}{k_{10} + k_{01} + A}. \quad (14)$$

The measured a.c. fluorescence signal is given by $A\Delta n_1$, apart from instrumental factors of proportionality. The measured absorption signal is given by $q(n_0 + \Delta n_0)$. Therefore, the Y value becomes $Y = A\Delta n_1/q(n_0 + \Delta n_0)$.

Using equation (14) this expression may be rewritten as

$$Y = \frac{A}{k_{10} + k_{01} + A} = \frac{A}{(k_{10} + A)[1 + k_{01}/(k_{10} + A)]}. \quad (15)$$

It follows from equation (12) that $k_{01}/(k_{10} + A) = (n_1/n_0) \leq 3 \exp(-E_{ex}/kT)$. This inequality represents the fact that occupation of the excited state without external light beam is generally less than the Boltzmann equilibrium value when the metal concentration is low and the Y -value is relatively large. The ratio (n_1/n_0) is, therefore, at most of the order 10^{-4} for the Na D-doublet in flames with temperatures of about 2500 K.

The term $k_{01}/(k_{10} + A)$ can thus be neglected in the numerator of expression (15). Equation (15) reduces to $Y = A/(A + k_{10})$ which is the familiar expression used in the interpretation of our modulated fluorescence measurements (see equation 2).