ELECTRONIC EXCITATION OF Na BY VIBRATIONALLY EXCITED N_2

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SUMMARY

The collisional excitation of Na by vibrationally excited, but electronically ground state N_2, (N_2^+), has been studied. Nitrogen atoms were removed catalytically from the flow before mixing with Na atoms, and experiments showed that N_2 (A) was not present in the excitation zone in sufficient amounts to account for observed intensities. The data have been analyzed on the assumption that only those vibrational to electronic energy transfers which are resonant contribute significantly to the excitation of Na. An excitation cross-section of 100 Å^2 was determined for the excitation of the $3p$ level of Na by the most resonant vibrational transition of N_2, namely $v = 11 \rightarrow v = 3$. Order-of-magnitude estimations of excitation rate constants and cross-sections have been made for the higher excited states of Na. The ratios of excitation and overall quenching rate constants for these states were found to decrease with increasing energy defect, as might be expected if resonance effects are important.

I. INTRODUCTION

Electronic–vibrational energy exchange between Na and N_2 has been the subject of several theoretical and experimental investigations[1-12]. One of the most important questions arising out of these investigations has been whether or not the efficiency of the energy exchange is strongly dependent on the degree to which the electronic energy change in Na matches the vibrational energy change in N_2. In three recent theoretical studies of the quenching of Na($3p$) by N_2[6-8], it has been suggested that quenching cross-sections may not be sensitive to such energy matching. In fact, it is predicted that only one-half of the energy of Na($3p$) is converted to vibrational energy in N_2, the rest being distributed among rotational and translational modes. Polanyi and co-workers have obtained experimental evidence for such non-resonant transfers in the quenching of Hg* by CO[13] and NO[14].

Although the cross-section for the quenching of Na(3p) by N_2 has been determined by a number of investigators[9-12] the experimental methods employed were not capable of distinguishing the vibrational levels of N_2 which were involved. Thus no evidence was brought forth which could be used to test the energy matching hypothesis. Experiments on the excitation of Na* by vibrationally excited N_2, (N_2^+)[2-5], have been largely qualitative in nature. The most important exception is the molecular beam study of Krause and Fite[3], in which a beam of N_2^+ was crossed with a beam of Na and the resulting Na-D emission intensity was measured. By using velocity selectors on both beams, they were able to correct for the contribution of the relative kinetic energy of the beam to the formation of Na(3p) and concluded that the excitation proceeded predominantly by way of:

$$Na(3s) + N_2(v = 11) \rightarrow Na(3p) + N_2(v = 3) \tag{1}$$
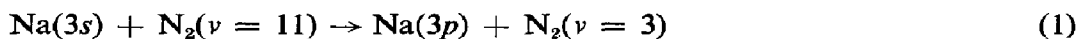
Since the $v = 11 \rightarrow v = 3$ transition in N_2 is the one which is the most resonant with the 3p level of Na, they concluded that the excitation cross-section must fall sharply with the energy defect; i.e. with the difference between the available vibrational energy and the excitation energy of Na(3p). The cross-section of reaction (1) was found to be 100 Å^2 and 200 Å^2, depending on how they corrected for relative beam velocities. Resonance effects have also been reported by Tsuchiya and Kuratani[4], who studied the emission of the Na-D lines in a shock-wave of N_2 seeded with Na.

In the work of Krause and Fite, there can be little doubt that Na(3p) was being excited by N_2^+ rather than by $N_2(A)$; i.e. N_2 in the $A^3\Sigma_u^+$ state. On the other hand, $N_2(A)$ may have contributed to the stimulation of Na emissions in the experiments of Starr[2] and of Milne[5], who observed these emissions on adding Na to flowing N_2 afterglows, which apparently showed the typical Lewis–Rayleigh bands of N_2. The presence of N was thereby indicated, and $N_2(A)$ was likely formed as the result of gas phase recombination of N[15]. Electronic–electronic transfer of energy from $N_2(A)$ to Na may have produced Na*. No evidence appears to have been published to indicate that this process is efficient; however, it should be regarded as at least a likely one, since Brennen and Kistiakowsky[15] have found evidence that Hg and other metallic atoms can be strongly excited by $N_2(A)$ in a flowing N_2 afterglow.

In view of this possibility, it is preferable to study the excitation of Na* by N_2^+ in the absence of N atoms. As stated above, this precaution was not taken by Starr and Milne, and as a result possible ambiguities may have been introduced into some of their conclusions. For example, both investigators found that the addition of N_2O to their active N_2 flows reduced the Na emission intensity. This was attributed to the deactivation of N_2^+ by N_2O, and was taken to indicate that Na* was being formed by N_2^+ only. However, since $N_2(A)$ is also readily quenched by N_2O[16], this conclusion appears to be open to question.

The present study was undertaken as a further test of the role of energy match-

ing or resonance in the excitation of Na* by N_2^+. Measurements were made of the Na emission intensity produced by mixing a Na bearing flow of argon with a flow of active N_2. To avoid possible ambiguities arising out of the presence of N atoms these were removed from the active N_2 before mixing with Na. Experiments were also done to show that $N_2(A)$ did not play an important role in the excitation of Na*.

II. EXPERIMENTAL

Figure 1 is a schematic diagram of the principal sections of the flow system used. The reaction tube was made of 50 mm o.d. Pyrex tubing, and the discharge tube of 13 mm o.d. quartz tubing. The reaction tube was isolated from the strong emissions produced in the discharge by a double Wood's horn located between the discharge and reaction tube. In addition, the discharge tube was wrapped in photographic black cloth. High purity nitrogen (Matheson Pre-purified) was passed through a sodium vapour trap for further purification and then through a microwave discharge in a tuned Evenson Cavity (2450 Mc/s; 85 W). The sodium vapour was transported to the reaction zone in an argon stream, also purified by passage through a sodium vapour trap. The sodium metal was initially freed of its oxide layer by cutting under xylene, then placed on a glass sleeve which was inserted into the reaction tube. Any remaining oxide layer was broken open by heating with a torch after evacuation of the system and the exposed metal was subsequently distilled downstream in the argon flow for purification while being heated by the sliding furnace. The sodium was distilled twice. Care was taken to remove any sodium films inadvertently distilled into the observation section during the purification by heating that section *in vacuo* overnight.

The system was evacuated by a Welch 1397 pump (425 1/min). All gas flows were measured with calibrated ball flowmeters and the pressure was measured with a mercury McLeod gauge placed at the downstream end of the reaction tube.

Observations were made at right angles to the flow at a point 40–70 cm downstream of the discharge and about 10 cm beyond the mixing zone. An ex-
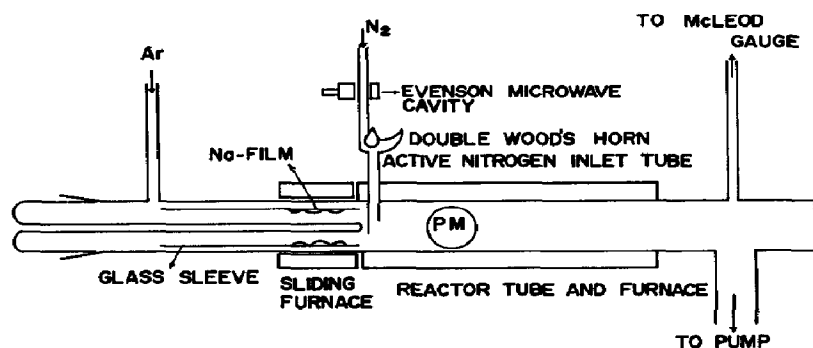

Fig. 1. Schematic diagram of reaction tube.

ponential decay of the emission intensity about the observation point was taken as evidence that mixing was complete at this point. Both absolute and relative intensity measurements were made. Absolute measurements were made with a RCA 1P28 photomultiplier whose field-of-view was defined by two adjustable slits. A 20 Å wide narrow band pass interference filter, peaked at 5904 Å, was placed between the slits on a rotatable mount, which permitted the filter to be tuned to the desired wavelength. The system was calibrated absolutely at 5893 Å against a NO–O afterglow according to the method outlined by Fontijn et al.[17]. This calibration was verified by one carried out against a G.E. quartz–iodine standard lamp. Relative measurements of intensities were made with a Jarrell-Ash 0.5 m Ebert mounted monochromator fitted with a EMI 9558QB photomultiplier. A ribbon filament standard lamp was used to calibrate the monochromator and photomultiplier over the spectral range 3000–8200 Å.

A total of sixteen resolved lines have been observed between 3300 and 8200 Å in the S, P and D series. These lines cover a range of principal quantum numbers from 3 to 11, and a range of excitation potentials from 2.1 to 5.0 eV. The S and D series were observed to the ionization limit of transitions terminating in the $3p$ level. Even under essentially "thin emitter" conditions, twelve sodium doublets could be resolved easily with the 0.5 m monochromator for quantitative measurement.

To determine absolute excitation cross-sections it was necessary to determine the concentration of Na, [Na], the concentration of excited Na, [Na*], and the concentrations of vibrationally excited N_2, [N_2^+]. The quantity, [N_2^+], can be determined if [N_2] is known together with the vibrational temperature, T_v, of N_2. Measurements of the partial pressure of N_2 and of the gas temperature were used to calculate [N_2]; however, T_v could not be measured independently, but was obtained from the treatment of the data as discussed later.

The absolute concentration of Na was determined as follows. In an optically thick slab of emitting Na, the intensity ratio of the Na-D lines should be less than the theoretical ratio of 2/1. The intensity ratio should vary with [Na] and the geometrical thickness of the slab, if the slab is uniform and if the kinetic temperature is kept constant. Procedures outlined by Mitchell and Zemansky[12], and Penner[18] may be used to calculate the intensity ratio of the Na-D lines as a function of [Na] and the geometrical thickness of the radiating slab, if the additional assumption of Doppler broadening is made. By means of these calculations it was possible to determine [Na] for the experimental path length from measured intensity ratios.

To test this method, the effective optical thickness was doubled by placing a plane mirror behind the reaction tube. The intensity ratio was measured and [Na] was calculated from this ratio. This value was then compared to [Na] obtained without the mirror; i.e. for a single pass. In a typical test run, a single pass measurement gave an intensity ratio of 1.86, from which [Na] was calculated to be 1.72×10^{10} particles cm^{-3}. For the double pass, the intensity ratio was found to be

1.795, from which was calculated, [Na] = 1.53 × 10^{10} particles cm^{-3}. The small discrepancy of 12% between these two values may be partly accounted for by the fact that in the single pass experiment about 5% of the radiation was reflected by the rear wall of the slab and passed through the slab twice. This would decrease the intensity ratio of the Na-D components by the same amount as would increasing [Na] by about 10%. In the double pass experiment, whether the emitted light is doubled back through the radiating slab by both the reaction tube wall and the mirror or by the mirror alone makes no difference, since in either case, the effect is to double the absorbing path.

To avoid unnecessary corrections for self-absorption, [Na] was kept low enough to assure near "thin emitter" conditions at 5893 Å. On the other hand, [Na] had to be sufficiently large to permit meaningful estimates to be made of it. For these reasons experiments were done under conditions for which the intensity ratio was approximately 1.90. The intensity ratios of the non-resonant lines are expected to be exactly 2/1, since no self-absorption occurs. These intensity ratios were measured for all the experiments done in the present study, and an average value of 2.00 ± 0.8% was obtained. This uncertainty in estimating the intensity ratio reflects an uncertainty in [Na] of ± 20%.

Absolute concentrations of all observed excited states of Na were obtained as follows. The absolute intensity, I^λ_{abs}, in W cm^{-3} emitted by Na* at the wavelength λ is related to [Na*] in particles cm^{-3} by:

$$I^\lambda_{abs} = \frac{hcA}{\lambda} [Na^*] \qquad (2)$$

Here, A is the Einstein A coefficient for the excited state.

Relative measurements of intensity, I^λ_{rel}, were made for all the strongest lines of Na, whereas I^λ_{abs} was measured only for the Na-D lines taken together. Absolute intensities were calculated from $I^\lambda_{abs} = (I^\lambda_{rel}/I^{5893}_{rel}) I^{5893}_{abs}$, and [Na*] was determined by setting such absolute intensities into eqn. (2). Values of A coefficients were taken from the tables of Wiese et al.[19].

For reasons discussed earlier in the paper, N atoms were removed from the active N$_2$ flow before mixing with the Na bearing argon flow. This was accomplished as follows. During the distillation of the sodium, a deposit, probably a mixture of sodium and its oxides, was always found to form on the active N$_2$ inlet tube. The Lewis–Rayleigh afterglow was completely quenched by the deposit, and the absence of any measurable afterglow downstream of the deposit was taken as an indication that only insignificant amounts of N penetrated into the reaction tube. This makes it unlikely that N$_2$ (A) was formed within the reaction tube.

The following experiment was done to assess the possible contribution to the Na emission from the N$_2$ (A) that may have formed either in the discharge or as the result of gas phase recombination of N in the active N$_2$ inlet tube between the discharge and the deposit. The system was thoroughly cleaned and a clean glass wool

plug was inserted into the active N_2 tube downstream of the Wood's horn. When flowing N_2 was subjected to a discharge the Lewis–Rayleigh afterglow was noticed downstream of the plug, and it was concluded that N was penetrating the plug in considerable amounts. Sodium was then loaded into the system, and purified by distillation in the usual manner. Subsequently it was found that N penetrated to the deposit formed during the distillation, but not beyond, and the Na emission was reduced to 10^{-3} of its normal value.

It is apparent, then, that the plug must have removed any energetic metastable molecules formed within the discharge from the active N_2 that may have been capable of exciting Na*. Because the Na intensity was so low, any N_2 (A) formed between the plug and the deposit was either removed from the flow by wall deactivation or did not contribute significantly to the excitation of Na*. On the other hand N_2^+ was probably not formed to any considerable extent within this section, since it is relatively insensitive to wall deactivation[20,21] and so would have been capable of reaching the reaction tube and exciting the Na there.

From these experiments it was concluded that the active species responsible for exciting Na* most probably were formed within the discharge. Any N_2 (A) formed within the discharge most likely did not reach the reaction tube in significant amounts, since the experiments with the glass wool plug showed that N_2(A) formed further downstream did not reach the reaction tube either. In a recent study, Brennen and Kistiakowsky[15] estimated that N_2(A) had a lifetime of, at most, 1 msec in a N_2 afterglow flowing through a 14 mm o.d. quartz tube with a linear speed of 10 m/sec. This time is of the order of that required for the N_2(A) to diffuse from the centre of the tube to the walls, and indicates that the N_2(A) was destroyed within 1–2 cm of its point of formation. Observations in the present study were made 40–70 cm downstream of the discharge. On the other hand N_2^+ has been observed by many investigators[20–22] at great distances downstream of N_2 discharges under conditions similar to those of the present study. Thus it is very likely that N_2^+ was the only species to excite Na* in the present study.

III. RESULTS

If the excited states of Na are in thermal equilibrium, eqn. (2) may be re-written:

$$I = (hc/\lambda)A(g_*/g)[\text{Na}] \exp(-E^*/kT^*) \tag{3}$$

where g and g_* are degeneracies of the ground and excited states of Na, respectively,

E^* is the excitation energy of Na*, and

T^* is the excitation temperature.

A plot of ln $(I\lambda/g_* A)$ vs. E^* should be a straight line with a slope of $-1/kT^*$. Figure 2 is such a plot for a typical experiment. It is obvious that the distribution
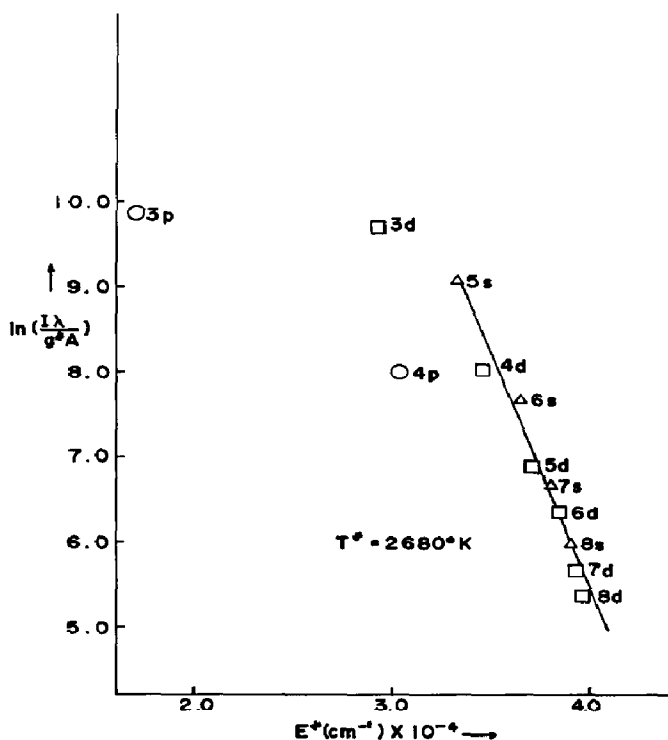
Fig. 2. Ln $(I\lambda/g_*A)$ *versus* excitation energy, E^*, for relative intensity measurements.

of excited states is non-Boltzmannian for this experiment. However, a straight line can be fitted reasonably well to points on the extreme right-hand side of the graph. For these an "excitation temperature" of 2680 K is indicated. Points for the 3p, 4p and 3d states do not fall on the line.

Milne[5] observed a similar non-equilibrium distribution with two significant differences. In the first place his excitation temperatures fell into the range 4000–4600K and were thus considerably higher than those observed in the present study. Secondly, in plots similar to Fig. 2, the 4p point was found by him to lie on the straight line. In the present study, in order to make the 4p point colinear with the other points on the right-hand side of Fig. 2, it would have to lie above the 3p and 3d points even though the energies of the 3p and 3d states lie below that of the 4p state. Such a shift in the 4p point would be considerably greater than the uncertainty in the intensity measurements.

Differences between the present results and Milne's may be explained perhaps by differences in experimental conditions. As mentioned earlier, in the present study, experiments were carried out in the absence of N atoms and N$_2$(A) was shown not to contribute significantly to the excitation of Na*, whereas both of these species likely were present in Milne's experimental system.

Figure 3 is a plot of ln[Na*] *vs.* E^*, where [Na*] is the absolute population of Na* determined as previously discussed. The data could be best fitted by two
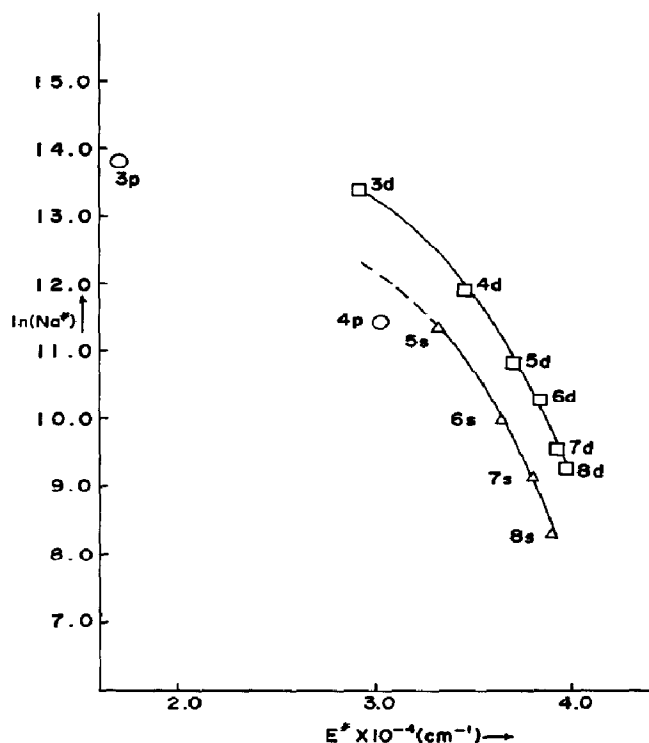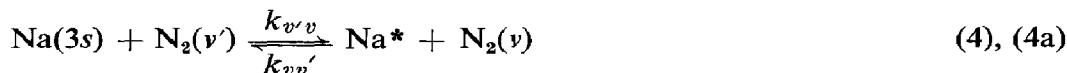
Fig. 3. Absolute populations of excited states of Na as a function of E^*.

curves—one for the d levels and one for the s levels. No curve was fitted through the p level points. Additional data for higher p levels could not be obtained, since the ultra-violet emissions from these states was absorbed by the Pyrex reaction tube used.

The following reaction mechanism was considered in interpreting the measured intensities of the Na emissions:

$$Na(3s) + N_2(v') \underset{k_{vv'}}{\overset{k_{v'v}}{\rightleftharpoons}} Na^* + N_2(v) \qquad (4), (4a)$$

$$Na^* + N_2 \overset{k_q}{\rightarrow} Na + N_2^{\ddagger} \qquad (5)$$

$$Na^{**} \overset{A'}{\rightarrow} Na^* + h\nu \qquad (6)$$

$$Na^{**} + N_2 \overset{k_c}{\rightarrow} Na^* + N_2^{\ddagger} \qquad (7)$$

$$Na^* \overset{A}{\rightarrow} Na + h\nu \qquad (8)$$

Here $N_2(v')$ and $N_2^{\ddagger}$ refer to vibrationally excited N_2 in the ground electronic state. $N_2(v)$ may refer to N_2 in either ground or excited vibrational levels. In reaction (4) and (4a), it has been assumed that Na^* is produced predominantly by collisions involving energy transfers with the lowest energy defect, ΔE, where $\Delta E = (E_{v'} - E_v) - E^*$. This assumption extends the conclusions of Krause and Fite[3] regarding resonance in the excitation of Na(3p) to all the excited states of Na. Reaction

(5) is the overall quenching reaction for Na* and includes reaction (4a) as a contributing member. The states of excitation of N$_2^+$ are not stipulated in this reaction, since these do not enter into the kinetic analysis. Radiative and "collisional" cascading to Na* from higher excited states of Na are accounted for by reactions (6) and (7), both of which must be summed over all excited states contributing to [Na*] in this way. Reaction (8) is for spontaneous emission from Na* to lower electronic states and must be summed for all of these transitions.

If reaction (7) is omitted from the mechanism, the data of the present study yield a cross-section of about 100 Å^2 for reaction (1), which compares favourably with the values obtained by Krause and Fite[3] for the same reaction under conditions in which reaction (7) could not have been very important. A detailed assessment of the significance of reaction (7) in the present study must await the determination of suitable cross-sections. For the present analysis, reaction (7) has been omitted.

Under steady-state conditions with regard to Na*:

$$[Na*] = \frac{k_{v'v}\,[Na(3s)][N_2(v')] + \Sigma_n\,A'_n\,[Na^{**}]_n}{\Sigma_i\,A_i + k_q[N_2]} \quad (9)$$

The second term of the denominator on the right-hand side of eqn. (9) gives the contribution of radiative cascading to the rate of formation of Na*. To estimate what fraction of [Na*] arises from cascading it is necessary to know k_q. This has only been measured for the 3p level; however, Bauer et al.[7] have calculated that $k_q(4p) = 2k_q(3p)$. Consideration of potential energy surfaces leads one to believe that quenching rate constants increase with E^* at a rate that is faster than linear. In view of this and in the absence of contrary evidence, it was decided to test the appropriateness of the relationship, $k_q(E^*) = k_q^o \exp(E^*/B)$, in interpreting the results of the present experiments. The quantities, k_q^o and B, are adjustable parameters. For the 3p level, E^* is about 1.697×10^4 cm^{-1} and k_q is calculated to be 2.62×10^{-10} cm^3 particle^{-1} sec^{-1} from a quenching cross-section of 34.2 Å^2 that is the average of several reported values[9-12]. For the 4p level, E^* is about 3.03×10^4 cm^{-1}, and k_q is taken to be 5.24×10^{-10} cm^3 particle^{-1} sec^{-1}. These values were used to solve for k_q^o and B, and the above relationship was re-written as:

$$k_q(E^*) = 1.09 \times 10^{-10} \exp(E^*/1.921 \times 10^4) \quad (10)$$

Calculations show that about 60% of the observed [Na(3p)] must have arisen from cascading from higher s and d states. For example, consider the experiment from which Fig. 3 was obtained. Absolute intensity measurements indicate [Na(3p)] = 10.1×10^5 particles cm^{-3}, and pressure measurements indicate [N$_2$] = 2.04×10^{16} particles cm^{-3}. Calculations based on [Na*] for s and d states taken from Fig. 3, together with tabulated A coefficients[19] and the value for $k_q(3p)$ given earlier show that 6.1×10^5 particles cm^{-3} arose from cascading. According to the proposed mechanism, reaction (5) must have contributed 4.0×10^5 particles

cm^{-3} to [Na(3p)]. Similar calculations showed that more than 90% of Na(4p) probably arose from cascading. Because of this no attempt was made to determine excitation cross-sections for Na(4p).

Cascading to s states occurs from higher p states. The populations of these were not determined experimentally, but were calculated with the help of Fig. 2 and eqn. (2). It was assumed that for these states $\ln(I\lambda/g_*A)$ fell on the straight line in Fig. 2. In this way a hypothetical relative intensity was calculated and was used to calculate absolute populations by the method described in the Experimental section. With these populations, tabulated A coefficients and k_q obtained from eqn. (10), it was calculated that $n'p{\rightarrow}ns$ transitions were probably not an important factor in populating s states. Since the 3p level was "underpopulated" with respect to the others (see Fig. 2), this calculation probably overestimates cascading to s states.

Cascading to d states involves $n'p{\rightarrow}nd$ $(n'>n)$ and $n'f{\rightarrow}nd$ $(n'{\geqslant}n)$ transitions. Calculations based on the [Na(n'p)] estimated above suggest that $n'p{\rightarrow}nd$ cascading was not significant. Since f level populations were not measured, these were calculated from [Na(nf)] = 1.4[Na(nd)], where 1.4 is the ratio of the degeneracies of f and d states. This is based on the fact that f and d states of the same principal quantum number have almost exactly the same energies. With the aid of these populations together with A coefficients calculated according to Anderson and Zilitis[23] it was possible to calculate that $n'f{\rightarrow}nd$ cascading played a minor role in populating d levels. The greatest contribution was approximately 20% to the 3d level; however, this had a negligible effect on the analysis to be discussed below.

The volume emission rate for transitions from s and d states can be written:

$$I = \frac{hcA\,[Na^*]}{\lambda} = \frac{hcAk_{v'v}}{\lambda}\,\frac{[Na(3s)]\,[N_2(v')]}{\Sigma_i\,A_i + k_q[N_2]} \tag{11}$$

The rate constants, $k_{v'v}$ and $k_{vv'}$, are related by $k_{v'v} = (g_*/g)k_{vv'}\,\exp(-\Delta E/kT) = (g_*/g)k_{vv'}$ for high T. For convenience in representing the data, $(g_*/g)k_{vv'}$ was substituted in eqn. (11) for $k_{v'v}$. For all "excitation temperatures" encountered in the present study [Na(3s)] may be replaced quite accurately by [Na]. With the additional assumption of Boltzmannian equilibrium for the vibrational levels of N_2, the following equation may be derived from eqn. (11):

$$X = \frac{I\lambda\{1 + (\Sigma_i A_i/k_q[N_2])\}}{g_*A} = \frac{hc[Na]}{gQ_v}\left(\frac{k_{vv'}}{k_q}\right)\exp(-E_{v'}/kT_v)$$

Here Q_v is the vibrational partition function for N_2 at temperature, T_v, and $E_{v'}$ is the energy of the vth vibrational level. It follows that:

$$\ln X = \ln\ \{hc[Na]/gQ_v\}\ + \ln(k_{vv'}/k_q) - E_{v'}/kT_v \tag{12}$$

The first term of the right-hand side of this equation is a constant for a given experiment. Provided that the second term does not change greatly from spectral
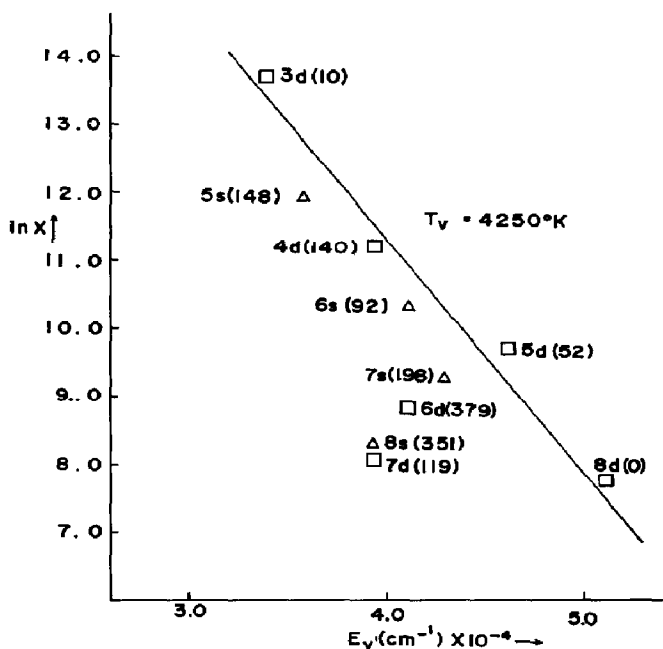
Fig. 4. Ln X versus $E_{v'}$ the energy of the upper vibrational level in the most resonant vibrational-electronic energy exchanges.

line to spectral line, a plot of ln X vs. $E_{v'}$ should give a straight line of slope $(-1/kT_v)$. Figure 4 is such a plot for the experiment illustrated by Fig. 2. Relative intensities were used to calculate X in this plot. A straight line fit seems to be quite appropriate for points having small values of ΔE. Points with large ΔE lie considerably below the line. One point, for the $7d$ level, is low even though ΔE is small. The scatter of the points having small ΔE about the line may arise partly from random error and partly from variations in $k_{vv'}/k_q$ with ΔE.

Figure 4 yields $T_v = 4250$K. For the excitation of Na($3p$) by reaction (1), the data of the run illustrated by Figs. 2 to 4 together with eqn. (11) yield $k_{11,3} = 7.8 \times 10^{-10}$ cm³ particle⁻¹ sec⁻¹, from which is obtained $\sigma_{11,3} = 1.0 \times 10^2$ Å². From a number of additional experiments in which T_v was allowed to vary from 3800 to 4500K, the following average constants were obtained: $k_{11,3} = 8.1 \times 10^{-10}$ cm³ particles⁻¹ sec⁻¹ and $\sigma_{11,3} = 1.05 \times 10^2$ Å². A mean deviation of a few percent testifies to the applicability of the treatment leading to eqn. (11).

The total expected error in $k_{11,3}$ was calculated to be $\pm 65\%$ from the following considerations. An expected error of $\pm 20\%$ has already been calculated for [Na] earlier in the report. An error of about $\pm 30\%$ in [$N_2(v = 11)$] is reflected by the 4% standard deviation of the low ΔE points about the straight line in Fig. 4. Additional errors of ± 1–2% in the measured pressure and of $\pm 10\%$ in the measured intensity also occurred. "Systematic" errors associated with the tabulated A coefficients have not been included in the error calculations.

At low T_v ($\sim$ 3000K), emissions arising from the higher excited states of Na were too weak to be measured sufficiently accurately to allow reliable fits to be made to ln X vs. $E_{v'}$ plots. To test the validity of the high temperature values of $k_{11,3}$ at these low temperatures, $k_{11,3} = 8.1 \times 10^{-10}$ was substituted into eqn. (11), and the ratio, $[N_2(v = 11)]/[N_2]$ was calculated from the data of the low temperature runs. From this ratio was calculated T_v, and attempts were made to fit straight lines of slope, $(-1/kT)$, through ln X vs. $E_{v'}$ plots for these runs. In all cases satisfactory fits were obtained.

To test the sensitivity of $k_{11,3}$ to the magnitude of k_q, Fig. 4 was replotted with k_q for all levels set equal to $k_q(3p)$. The effect of this was to reduce T_v by 100K and to increase $k_{11,3}$ and $\sigma_{11,3}$ by 20%. Thus the calculated values of these constants do not appear to be very sensitive to the assumed value of k_q and no gross errors appear to have resulted from the values assumed for k_q.

Table I lists $(\sigma_{vv'}/\sigma_q)$,$(k_{vv'}/k_q)$, $\sigma_{v'v}$, ΔE and the most resonant vibrational transitions in N_2. Figure 4 and eqn. (12) were used to calculate $\sigma_{vv'}/\sigma_q$. For this calculation, X had to be expressed in terms of absolute intensities. Calculations of $\sigma_{v'v}$ were based on $\sigma_{v'v}/\sigma_q$ and the two sets of assumed values of k_q previously discussed.

Table I shows that $k_{vv'}/k_q$ decreases with increasing ΔE. This is shown more strongly in Fig. 5. Points for both the s and d levels can be fitted with smooth curves satisfactorily. Since $k_{v'v}$ equals $(g_*/g) k_{vv'}$, $(k_{v'v}/k_q)$ should depend on ΔE in the same way as $(k_{vv'}/k_q)$.

In the calculation of rate constants it has been assumed that the excitation of all higher states of Na occurs predominantly by way of the most resonant vibrational transition to N_2. To test this, Fig. 5 was used to calculate $(k_{v'v}/k_q)$ for other vibrational transitions capable of exciting a given electronic state of Na.

TABLE I

EXCITATION AND QUENCHING CROSS-SECTIONS FOR Na*

State	$v'-v$	ΔE (cm^{-1})	$\sigma_{vv'}/\sigma_q$ $(k_{vv'}/k_g)$		$\sigma_{v'v} \times 10^{-2}$ (Å^2)	
			(a)	(b)	(a)	(b)
$3p$	11–3	166	1.0	1.2	1.0	1.2
$5s$	17–1	148	3.4	6.0	2.7	2.1
$6s$	20–2	92	4.1	7.3	3.5	2.5
$7s$	21–2	198	2.5	4.6	2.6	1.6
$8s$	19–0	351	0.33	0.49	0.35	0.17
$3d$	16–2	10	7.8	15	25	26
$4d$	19–2	140	4.6	10.2	21	18
$5d$	23–4	52	11.5	20.3	56	35
$6d$	20–1	379	0.81	1.84	4.3	3.1
$7d$	19–0	119	0.22	1.24	1.2	2.1
$8d$	26–5	0	8.9	15.7	50	27
$9d$	25–4	266	2.9	4.2	16	7.2

(a) Assuming k_q as given by eqn. (10).
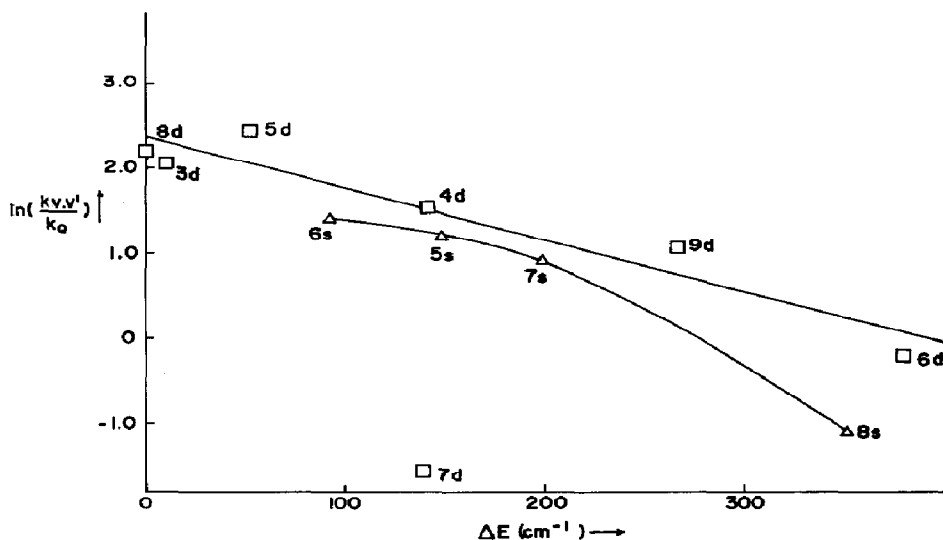(b) Assuming k_q to be 2.42 $\times$ 10^{-10} cm^3 particle^{-1} sec^{-1} for all levels.

Fig. 5. $k_{vv'}/k_q$ as a function of energy defect, ΔE.

Rates of excitation were then calculated for these transitions and compared to the rate associated with the most resonant transition. For example, the $4d$ level can be excited by both the 18-1 and 23-5 transitions, in addition to 19-2, the most resonant one. These transitions have energy defects of 636, 324 and 140 cm^{-1} in the order listed. Figure 5 gives $(k_{18,1}/k_q) = 0.21$, $(k_{23,5}/k_q) = 1.46$ and $(k_{19,2}/k_q) = 4.6$. Since k_q has the same value for all of these transitions, the rate of formation of Na($4d$) is proportional to $R_{v'v}$, where $R_{v'v} = (k_{v'v}/k_q)[N_2(v')]$. At $T_v = 4500$K, the highest temperature in the present study, $R_{18,1} = 1.3 \times 10^{-6}$, $R_{23,5} = 0.57 \times 10^{-6}$ and $R_{19,2} = 22 \times 10^{-6}$. At $T_v = 3000$K, the lowest temperature, $R_{18,1} = 3.4 \times 10^{-9}$, $R_{23,5} = 2.5 \times 10^{-13}$ and $R_{19,2} = 31 \times 10^{-9}$. It is evident that the 19-2 transition predominates, as was assumed. Similar calculations for the other levels demonstrated the predominance of the most resonant transition in all cases.

Quenching of Na* by reaction (4a) cannot occur more rapidly than by reaction (5), the overall quenching reaction. If the values of $k_{vv'}/k_q$ listed in Table I are to be consistent with this requirement, the following condition must be met: $(k_{vv'}/k_q)Q_v^{-1} \exp(-E_{v'}/kT_v) \leqslant 1$. At $T_v = 3000$K, the inequality holds exactly for all electronic states. At $T_v = 4500$K, the inequality holds exactly for all electronic states, except for those d levels that have the highest values of $k_{vv'}/k_q$. For these levels, the left-hand side of the inequality ranges in value from 1 to 1.5. This is not unreasonable, since $k_{vv'}/k_q$ cannot be determined with greater than order-of-magnitude certainty.

Some values of $\sigma_{v'v}$ in Table I are as high as 5×10^3 Å^2. Such high cross-sections have been reported previously in the scientific literature. For example, Rautian and Khaikin[24] have suggested a quenching cross-section of 10^4 Å^2 to account for the low observed emission intensity from Na ($8p$) produced by colli-

sions between $Na(3s)$ and $Hg(6^3P)$. It is difficult to imagine interactions occurring at the great distances implied by such large cross-sections.

The values of $\sigma_{v'v}$ listed in Table I, apart from $\sigma_{11,3}$ must be regarded as provisional, since they were calculated from assumed values of k_q. In addition, the role of reaction (7) in populating higher excited states should be examined. This was beyond the scope of the present study, unfortunately.

Milne[5] has proposed that T^* for Na should be equal to T_v for N_2. According to this proposal, T_v, for the run illustrated in Figs. 2 to 4, should be 2680K (see Fig. 2) and not 4250K (see Fig. 4). For such a low temperature, eqn. (11) applied to the experimental data yields $k_{11,3} = 8.4 \times 10^{-8}$ cm³ particles⁻¹ sec⁻¹ and $\sigma_{11,3} = 1.09 \times 10^4$ Å². This cross-section is about 50 times as great as the values obtained by Krause and Fite[3]. It would therefore appear that Milne's proposal is not consistent with the choice of reaction (1) as the dominant reaction in the excitation of $Na(3p)$.

Milne's proposal was also tested for non-resonant vibrational–electronic transfer. In this case, the excitation would be given by

$$R = [Na]\,\Sigma_j k^j_{v'v}\,[N_2(v')]_j = \frac{[Na][N_2]}{Q_v}\,\Sigma_j[k^j_{v'v}\exp\,(-E^j_{v'}/kT_v)]$$

where the summation is to be carried out for all vibrational transitions with enough energy to excite Na*. This equation can be re-written in terms of k_{av} where k_{av} is a rate constant that is averaged over all contributing vibrational transitions according to:

$$k_{av}Q^{-1}_v\,\Sigma_j \exp\,(-E^j_{v'}/kT_v) = Q^{-1}_v\,\Sigma_j k^j_{v'v}\exp\,(-E^j_{v'}/kT_v)$$

$$\therefore R = [Na][N_2]k_{av}Q^{-1}_v\,\Sigma_j \exp\,(-E^j_{v'}/kT_v), \qquad (13)$$

$$\text{and } [Na^*] = [Na][N_2]k_{av}Q^{-1}_v\,\Sigma_j \exp\,(-E_{v'}/kT_v/\{\Sigma_i A_i + k_q[N_2]\}$$

For the $3p$ level, k_{av} and σ_{av} were calculated to be 1.38×10^{-9} cm³ particle⁻¹ sec⁻¹ and 180 Å² respectively, by applying eqn. (13) to the data of the run represented in Fig. 2. These values are reasonable; however, for the $3d$ level σ_{av} is calculated to be 10^5 Å² and for the $8d$ level σ_{av} is calculated to be 10^6 Å². These values are unacceptably large.

Arguments and evidence have been presented in the present report in support of the hypothesis that in the system, Na plus N_2^+, the transfer of vibrational energy from N_2^+ to Na in the form of electronic energy is a resonant process, requiring close matching between the available vibrational energy and the energy of the excited electronic state. In the excitation of $Na(3p)$, this hypothesis leads to a value of about 100 Å² for the cross-section of reaction (1), which is in satisfactory agreement with the lower of the values of the same cross-section obtained by Krause and Fite[3] in a crossed beam experiment. Provisional order-of-magnitude estimates of excitation cross-sections have been made for other excited states of

Na; however, these estimates were based on assumed values of quenching rate constants, and are not considered reliable.

The conclusions of the present study are subject to three main assumptions, apart from the proposed mechanism.

(1). Thermal equilibrium was assumed for the vibrational levels of N_2.

(2). Reaction (7) of the proposed mechanism was ignored.

(3). Quenching rate constants were estimated for the higher excited states, since no experimental values exist.

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Note added in proof (7. 8. 72)

Since the submission of the present paper, Krause, Fricke and Fite[25] have re-analyzed the results of Krause and Fite[3] obtained from experiments in which a beam of Na was crossed with one of N_2^+. They prefer a mechanism in which an appreciable fraction of the energy required to excite Na(3p) comes from kinetic energy, with the remainder being made up by a variety of vibrational transitions in N_2^+. On the other hand, on assuming that a single vibrational transition only plays a significant role in the excitation process, they show that this "most probable" transition is also the most resonant one; namely $v = 11 \rightarrow v = 3$. The cross-section, $\delta_{11,3}$, for this transfer calculated by them agrees satisfactorily with the values of $\delta_{11,3}$ obtained in the present study.

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