

ELECTRONIC-EXCITATION TRANSFER COLLISIONS IN FLAMES—VI. INTERPRETATION OF THE TEMPERATURE DE- PENDENCE OF ALKALI-QUENCHING BY N₂ AND GENERAL CONCLUSIONS ABOUT THE ENERGY TRANSFER MECHANISM

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Abstract—The experimental temperature dependence of alkali-N₂ quenching cross sections is explained semi-quantitatively by a simple theoretical model, based on an ionic intermediate state, in which attractive van-der-Waals forces play an essential role. Using this model, quenching experiments are compared with Na(3²P)-N₂ excitation measurements in molecular beams. From this comparison it is concluded that the distribution of relative cross sections for specific vibrational transitions during the quenching process can be described by a distribution calculated by FISHER,⁽⁸⁾ whereas the distribution given by BJERRE⁽¹⁸⁾ has to be rejected. Resonant vibrational-electronic energy transfer is not important.

1. INTRODUCTION

THE INTERCONVERSION of electronic, vibrational, rotational and translational energy of the collision partners during alkali-molecule collisions, is still an unsolved problem.^(1–10) In particular, the importance of resonance effects in vibrational-electronic energy transfer is an unsettled question.

In this paper we try to interpret the available experimental alkali-N₂ quenching data by means of a simple theoretical model.^(6–9) Using this interpretation and applying detailed balance, we shall calculate the excitation rate constant that is measured in a crossed alkali-N₂ beam experiment and compare it with experimental results.⁽¹⁶⁾ This procedure enables us to draw additional conclusions about the kind of energy transfer involved. Finally we will discuss the question of resonance effects. For a survey and brief discussion of the relevant literature, we refer to other parts of this series^(1–4) and to Ref. (5).

2. THEORETICAL MODEL

BAUER *et al.*⁽⁹⁾ and FISHER and SMITH^(7,8) have developed a quantitative theoretical model for alkali-diatomic molecule quenching collisions, based on the assumption of an intermediate ionic state, which crosses both initial and final states of the collision complex. However, their calculations did not agree with the experimentally-determined temperature dependence.^(1,6,7) From the detailed results of Refs. (8) and (9), the following conclusion can be drawn. The quenching probability, $q(n)$, for all collision partners that are able to pass at a mutual distance shorter than $R_c(n)$, is virtually constant. Here $R_c(n)$ denotes the largest crossing distance on the initial potential-energy curve, and n the initial vibrational quantum-number. We now assume that this conclusion remains valid, when the van-der-Waals attraction is included on the initial potential-energy curve, which was neglected

in Refs. (7–9). This assumption was numerically checked to be valid. Our assumption requires that the relative translational energy of the collision partners, E , be sufficiently large, either to surmount the centrifugal barrier, if the barrier maximum is located at a mutual distance $R_m(n) > R_c(n)$, or to reach $R_c(n)$, if $R_m(n) < R_c(n)$. For a van-der-Waals-potential, $R_m(n)$ is given by $R_m(n) = (3C_6(n)/Eb^2)^{1/4}$, where b is the impact parameter and $C_6(n)$ is van-der-Waals-constant with the molecule in the n -th vibrational state and the atom in the excited state considered. The unknown n -dependence of C_6 will be neglected. We then obtain the following expressions for the quenching cross section:⁽¹⁰⁾

(a) for $E \leq 2C_6/R_c^6(n)$,

$$\sigma_{qu}(E, n) = q(n)\pi R_c^2(n)(3/2)^{2/3}(3C_6/ER_c^6(n))^{1/3}; \quad (1)$$

(b) for $E \geq 2C_6/R_c^6(n)$,

$$\sigma_{qu}(E, n) = q(n)\pi R_c^2(n)\{1 + C_6/ER_c^6(n)\}. \quad (2)$$

Thus, the existence of an attractive force leads to an explicit energy dependence. Furthermore $\sigma_{qu}(E, n)$ is a sum of cross sections for transitions from n to all possible n' , i.e.

$$\sigma_{qu}(E, n) \equiv \sum_{n'} \sigma_{qu}(E, n, n'). \quad (3)$$

In thermodynamic equilibrium, the measured effective cross section, $[\sigma_{qu}(T)]_{eff}$, is a Maxwellian average of the relative velocity times $\sigma_{qu}(E, n)$, divided by the average relative velocity.^(1,6) This Maxwellian averaging cannot be performed analytically for the energy range where equation (1) applies. However, in order to obtain the qualitative temperature dependence of $(\sigma_{qu}(T))_{eff}$, we apply equation (2) over the entire energy range. The resulting error is about 15 per cent at $T = 300$ K and negligible for $T > 600$ K. We obtain

$$(\sigma_{qu}(T))_{eff} = \sum_n \frac{e^{-E_n/kT}}{Q(T)} q(n)\pi R_c^2(n) \left\{ 1 - \frac{V[R_c(n)]}{kT} \right\}, \quad (4)$$

where k is Boltzman's constant, $Q(T)$ is vibrational partition function, E_n is energy of the n -th vibrational state and $V[R_c(n)] = -C_6/R_c^6(n)$.

FISHER and SMITH^(7,8) have found the product $q(n)\pi R_c^2(n)$ to be independent of n for all relevant n -values up to $T = 2500$ K ($n < 4$). Now, for a given ionic curve, $R_c(n)$ varies by less than 10 per cent when n varies from 1 to 4 and thus $V[R_c(n)]$ varies by less than 60 per cent for $n < 4$. Such a variation may be neglected, because at lower temperatures ($kT \approx 0.03$ eV) the higher excited vibrational states are negligibly populated, whereas at flame temperatures ($kT \approx 0.2$ eV) $V[R_c(n)]/kT$ is expected to be considerably smaller than unity. So, neglecting the n -dependence in equation (4) we get

$$[\sigma_{qu}(T)]_{eff} = q\pi R_c^2 \left[1 - \frac{V(R_c)}{kT} \right]. \quad (5)$$

Equation (5) shows an explicit T dependence as a result of the van-der-Waals-term. Because $V(R_c)$ and $q\pi R_c^2$ are unknown, we can fit equation (5) to the available experimental data.

3. COMPARISON OF QUENCHING EXPERIMENTS WITH THEORY

The most reliable experimental data^(1–5) for quenching of Na(3²P), K(4²P), Rb(5²P) and Cs(6²P) by N₂ have been plotted in Figs. 1–4, as a function of T . The values of the fitting parameters $q\pi R_c^2$ and $V(R_c)$, used for the drawn lines in these figures, are given in Table 1.

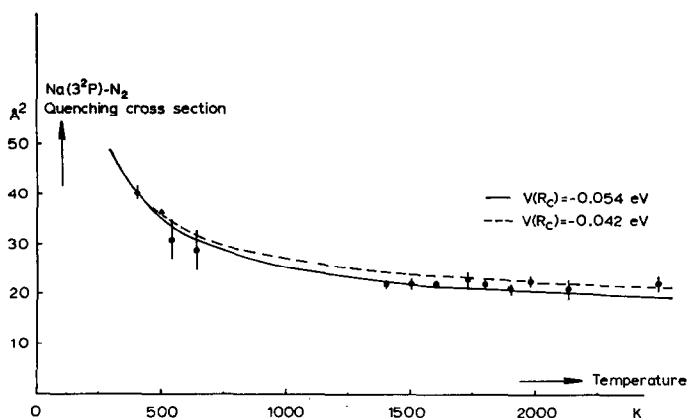


Fig. 1. Plot of the most reliable effective quenching cross sections for $\text{Na}(3^2\text{P})\text{-N}_2$, as a function of T , together with the theoretical temperature dependence (drawn curve) as obtained from equation (5), for two values of $V(R_c)$.

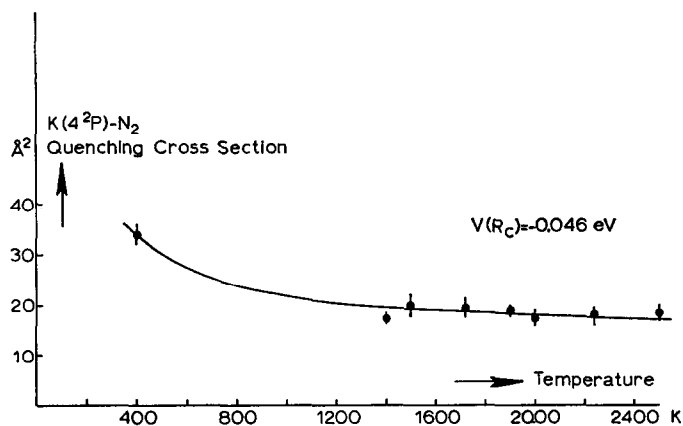


Fig. 2. Plot of the most reliable effective quenching cross sections for $\text{K}(4^2\text{P})\text{-N}_2$, as a function of T , together with the theoretical temperature dependence as obtained from equation (5).

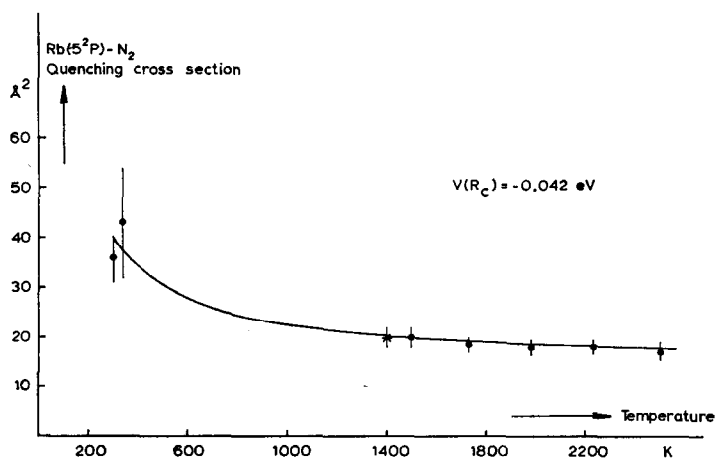


Fig. 3. As in Fig. 2, but for $\text{Rb}(5^2\text{P})\text{-N}_2$.

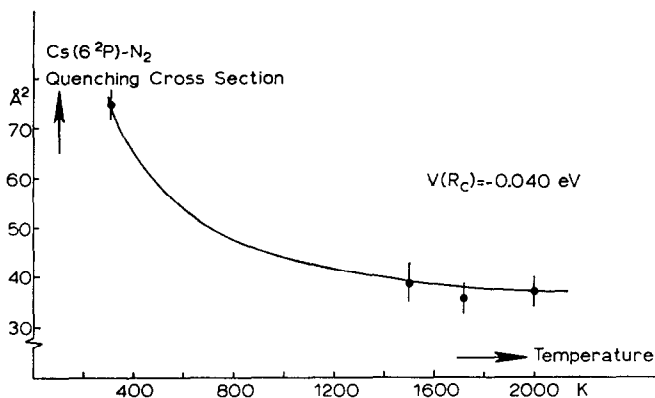


Fig. 4. As in Fig. 2, but for Cs(6²P)-N₂.

Table 1. Parameters used for fitting equation (5) to the experiments, as shown in Figs. 1-5. No significance should be attached to the trend in $V(R_c)$ going from Na to Cs, because of the qualitative nature of the procedure followed

Collision partners	$q\pi R_c^2$ (Å ²)	$V(R_c)$ (eV)
Na-N ₂	17.0	-0.050
K-N ₂	14.0	-0.046
Rb-N ₂	15.0	-0.042
Cs-N ₂	30.0	-0.040
Na-H ₂	6.0	-0.060

In all cases, a good fit between experiment and theory was obtained. Figure 1 shows two curves in order to demonstrate the sensitivity of the fitting procedure to a change in $V(R_c)$. Because of the qualitative character of the theoretical model, the systematic trend found in $V(R_c)$, from Na to Cs, is not necessarily meaningful, but the order of magnitude is reasonable. Thus, the ionic curve-crossing model, after inclusion of the attractive part of the interaction potential, can explain satisfactorily the temperature dependence of alkali-N₂ quenching cross sections. Recently the same conclusion has been drawn independently by ANDREEV⁽¹¹⁾ for K-N₂ quenching.

We also fitted equation (5) to Na-H₂ quenching experiments, as shown in Fig. 5. For K-H₂ quenching, a temperature dependence similar to that for Na-H₂ has been measured,⁽⁴⁾ except that the ratio of low-to high-temperature cross sections is about 3 for K-H₂, whereas it is about 2 for Na-H₂. Fitting equation (5) to the K-H₂ experiments yields $V(R_c) \approx -0.17$ eV, which is an unreasonably high value in this case. We conclude from this inconsistency and from the Rb-H₂ and Cs-H₂ experiments^(3,4) that our model is too simple to explain the H₂-results.

The reason for the success of the model in explaining N₂-quenching may be that, once the atom-molecule pair has reached the mutual crossing distance R_c , probably so many curve-crossings occur within the potential-energy 'grid' that quantum mechanical interferences are smoothed out. Then a classical diffusion calculation with roughly estimated

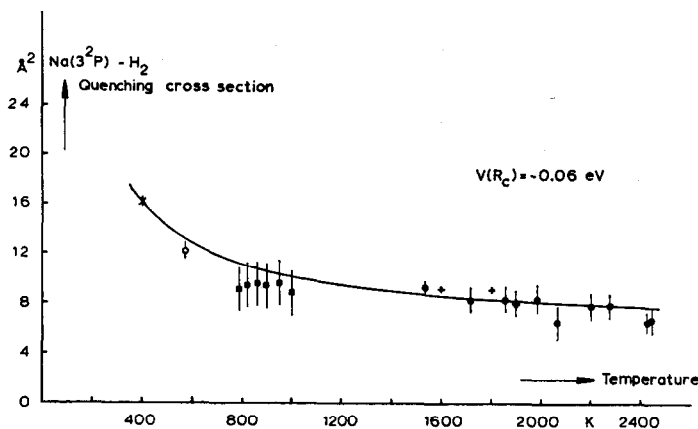


Fig. 5. As in Fig. 2, but for Na(3²P)-H₂.

parameters may work as well. WOOLLEY⁽¹²⁾ has shown, however, that a classical diffusion calculation is not applicable to a potential-energy grid involving only nine crossing points. This result suggests that the model calculations are better for N₂ or O₂ than for H₂. The expected stronger orientation dependence for alkali-H₂ than for alkali-N₂ interactions⁽¹³⁻¹⁵⁾ may also invalidate the model for H₂. It should also be realized that experimental data obtained in bulk systems are effective values, so that any detailed structure in the energy dependence of $\sigma_{qu}(E, n)$ is expected to smooth out.

New measurements on Na-N₂ quenching were published very recently, by BARKER and WESTON⁽²⁸⁾ These authors have measured σ_{qu} by photodissociating NaI with radiation of variable wavelength in a thermal N₂-environment. They found a decreasing cross section with increasing relative velocity. Their measurements were explained by a theoretical model similar to ours. However, an essential difference is that they interpreted $V(R_c)$ as half the energy splitting of a pseudo-crossing at R_c , instead of as being due to van-der-Waals forces.^(4,11) The value $V(R_c) \approx 0.2$ eV, as found in Ref. (28), is inconsistent with the difference between previously measured high- and low-temperature data^(1,6) We do not believe that the discrepancy between our flame data and the measurements of Ref. (28) can be fully explained by differences in internal energy distribution of N₂, as has been suggested.⁽²⁸⁾ This explanation would require an improbably strong dependence of quenching on the initial vibrational energy level since the gas temperature⁽²⁸⁾ in the experiment (900K) was only 500K lower than in the coolest flames (1400K).

4. THEORETICAL RELATION BETWEEN EXPERIMENTAL QUENCHING AND EXCITATION RATES

The principle of microscopic reversibility provides a relation between the cross section for a specific, detailed reaction path and that for the corresponding reversed reaction path. When, for simplicity, we neglect rotational transitions, the following relation holds for Na(3²P)-N₂ excitation and de-excitation reactions:

$$g_1 E' \sigma_{qu}(E', n, n') = g_0 E \sigma_{ex}(E, n', n), \quad (6)$$

where $g_{1,0}$ is the statistical weight of the electronically-excited state 1 and ground state 0, respectively; $\sigma_{qu}(E', n, n')$ is the quenching cross section for an electronic transition $1 \rightarrow 0$, accompanied by a vibrational transition from $n \rightarrow n'$, at initial relative translational energy

E' ; $\sigma_{ex}(E, n', n)$ is the excitation cross section for the exactly reversed process. The quantities E and E' are related by $E = E' + E_{n'n}$, where $E_{n'n} = E_{10} - (E_n - E_n')$ and E_{10} is the electronic excitation energy involved. $E_{n'n}$ is the minimum amount of relative translational energy required for excitation or released by quenching. It is assumed that no additional activation energy is required. Equation (6) can be rewritten as

$$\sigma_{ex}(E, n', n) = \frac{g_1}{g_0} \left(1 - \frac{E_{n'n}}{E}\right) \sigma_{qu}(E - E_{n'n}, n, n'). \quad (7)$$

In a thermal crossed-beam experiment, the excitation rate constant measured is given^(16,17) by

$$k_{ex} = \sum_{n, n'=0}^{\infty} \frac{e^{-E_{n'n}/kT_2}}{Q(T_2)} \int_{E_{n'n}}^{\infty} \sigma_{ex}(E, n', n) F(E) dE, \quad (8)$$

where T_2 is temperature of molecular beam, describing the initial vibrational-state population, $F(E)$ is the non-Maxwellian distribution function of relative translational energy. Substituting equation (7) into (8) and using equation (2), we obtain

$$k_{ex} = \sum_{n, n'=0}^{\infty} \frac{e^{-E_{n'n}/kT_2}}{Q(T_2)} \int_{E_{n'n}}^{\infty} q(n, n') \pi R_c^2(n) \frac{g_1}{g_0} \left\{1 - \frac{[E_{n'n} + V(R_c(n))]}{E}\right\} F(E) dE, \quad (9)$$

with

$$q\pi R_c^2 \equiv \sum_n q(n, n') \pi R_c^2(n) \quad (10)$$

because the n -dependence of $q(n) \pi R_c^2(n)$ can be neglected (see above). The parameters $q\pi R_c^2$ and $V(R_c)$ can be obtained from the quenching experiments (see above). The distribution, $q(n, n')$, of the respective vibrational transitions can be estimated from a comparison between calculated values of k_{ex} according to equation (9) and measured values of k_{ex} of KRAUSE *et al.*⁽¹⁶⁾ We calculated k_{ex} for three widely different trial $q(n, n')$ distributions. Such a comparison can give additional information, not contained in each experiment separately, due to the fact that, in a crossed-beam experiment, the internal energy distribution is described by a temperature, T_2 , which may differ considerably from the temperature which describes the relative translational energy distribution approximately. This observation may be contrasted with quenching measurements in flames and vapor bulbs, where the two temperature values are equal.

5. CONFRONTATION OF QUENCHING AND EXCITATION EXPERIMENTS

KRAUSE *et al.*⁽¹⁶⁾ have measured k_{ex} for Na(3^2P)-excitation in collisions with N_2 , H_2 and D_2 . A thermal Na-beam was crossed at right angles by a thermal diatomic-molecule beam. For Na- N_2 collisions, the temperature T_2 determining the vibrational energy distribution, is about twice the temperature describing approximately the relative translational-energy distribution. A further separation of the roles played by internal and translational degrees of freedom was obtained by velocity selection of the molecular beam. Thus, these authors were able to obtain excitation cross sections for specified vibrational transitions.

We calculated numerically the quantity $\eta(T_2)$ defined by $\eta(T_2) \equiv e^{E_{10}/kT_2} k_{ex}$, where k_{ex} is given by equation (9). Values for $q\pi R_c^2$ and $V(R_c)$ were taken from Table I. Although $q\pi R_c^2$ was taken to be independent of n , this need not to be true for the individual $q(n, n')$.

We first chose, for a trial estimate, relative $q(n, n')$ - values for Na(3^2P)-N₂ excitation, according to the calculations of FISHER and SMITH^(7,8) (as found for $E = 0.2$ eV and an ionic-complex polarizability $\alpha = 40 \text{ \AA}^3$).

An alternative calculation of η was done with relative $q(n, n')$ -values, as calculated theoretically by BJERRE.^(18,19) Finally, a third η -calculation was done while assuming a near-resonant electronic-vibrational energy transfer. The distributions $q(n, n')\pi R_c^2(n)$, as used in our three calculations of η , are shown schematically in Fig. 6 for $n = 0$.

Our calculated total excitation rate constants η are shown in Fig. 7, together with the measurements of KRAUSE *et al.*⁽¹⁶⁾

Curve 2 in Fig. 7 represents the calculated η for the Fisher-distribution of $q(n, n')$. The difference with experiment is within a factor 2 in the temperature range considered. Curve 3 shows the results of our calculations in the near-resonant case. This result is too large by about a factor of 8 at $T_{N_2} \approx 2100\text{K}$ and by about a factor of 3 at $T_{N_2} = 2800\text{K}$. Using the Bjerre-distribution, we found η to increase from $\approx 10^{-12} \text{ cm}^3\text{s}^{-1}$ at $T_{N_2} = 2000\text{K}$ to $\approx 3 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$ at $T = 2800\text{K}$, which is about a factor of 60–100 smaller than the experimental values. Therefore, we concluded that the Bjerre-distribution has to be rejected. In order to show the influence on $\eta(T_{N_2})$ of the translational energy dependence of σ_{qu} , according to equation (2), we also calculated η with the Fisher-distribution while using $V(R_c) = 0$ and $q\pi R_c^2 = 22 \text{ \AA}^2$ in equations (9) and (10). The result is shown as curve 1 in Fig. 7. The difference between curves 1 and 2 is obviously too small to draw conclusions as to the validity of equation (2) from excitation experiments. Inspection of Fig. 7 shows that a Fisher-like distribution agrees better with the experiments than do results obtained with the other two distributions. Even so it appears impossible to reproduce the suggested experimental temperature dependence of η , with any distribution compatible with the quenching experiments, without considerably reducing the agreement in absolute magnitude between calculations and experiments.

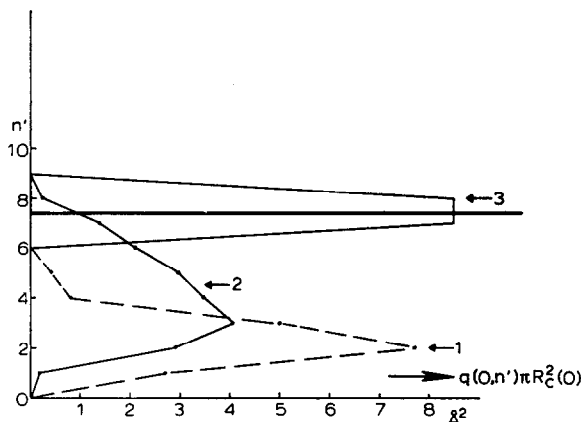


Fig. 6. The distribution function $q(n, n')\pi R_c^2(n)$, schematically plotted as a function of the final vibrational quantum number n' , for the initial vibrational quantum number $n = 0$. The distributions are normalized so that $\sum_n q(n, n')\pi R_c^2(n) \equiv q\pi R_c^2 = 17 \text{ \AA}^2$ matches the result obtained in quenching experiments. Distribution No. 1 is derived from Refs. (18) and (19), No. 2 from Ref. (8), whereas No. 3 refers to near-resonant vibrational-electronic energy transfer. The heavy line gives the position of the Na(3^2P)-excitation energy (2.1 eV).

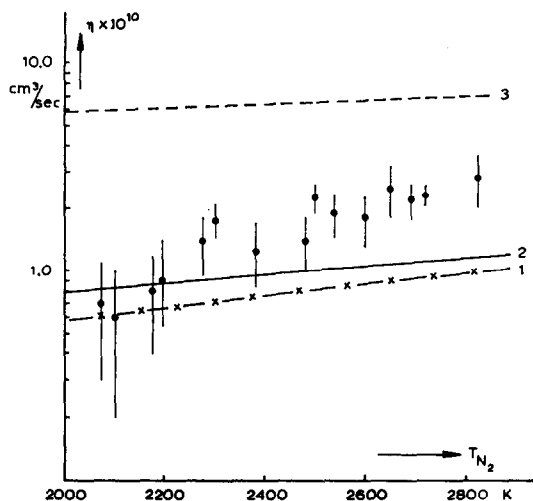


Fig. 7. Calculated and experimental $\text{Na}(3^2\text{P})\text{-N}_2$ excitation rate constants η , as functions of the N_2 oven temperature in a crossed molecular beam experiment. Experimental points have been taken from Ref. (16). Curve 1 gives our calculated η with $q(n, n')$ obeying to a Fisher-distribution (see Fig. 6) and an assumed E -independent quenching cross section, with $q\pi R_c^2 = 22 \text{ \AA}^2$. Curve 2 gives a calculated value for η with $q(n, n')$ again obeying a Fisher-distribution, but now assuming that the quenching cross section is given by equation (2). Curve 3 gives a calculated value for η when resonant vibrational-electronic energy transfer is assumed, according to distribution No. 3 in Fig. 6. The energy dependence follows again from equation (2). The calculated η , according to the Bjerre-distribution, is not shown in this figure, because it yields unrealistically low values of $\eta \approx 10^{-12} \text{ cm}^3/\text{sec}$.

In a separate velocity-selected measurement, KRAUSE *et al.*⁽¹⁶⁾ obtained values for certain excitation cross section sums, $\bar{\sigma}_{\Delta n}$, parametrized by the vibrational quantum number jump Δn (see Table 2). The absolute values of $\bar{\sigma}_{\Delta n}$ depend on the assumed translational-energy dependence of $\sigma_{ex}(E, n', n)$. In Ref. (16), $\bar{\sigma}_{\Delta n}$ -values were derived for two assumed energy

Table 2. Cross section sums for fixed Δn , are defined by

$$\bar{\sigma}_{\Delta n} \equiv \sum_{n'=\Delta n}^{\infty} \sigma_{n', n' - \Delta n} \frac{e^{-(E_{n'} - E_{\Delta n})/kT}}{Q(T)},$$

where $\Delta n =$ vibrational quantum jump in the excitation process, $E_{\Delta n} =$ jump in the vibrational energy corresponding to Δn , $\sigma_{n', n' - \Delta n} \equiv q(n', n' - \Delta n)\pi R_c^2(n')$. The measured and calculated values are taken at $T_{\text{N}_2} = 2600\text{K}$. Data in column II have been obtained while assuming $\sigma_{ex}(E, n', n) \equiv \sigma_{n', n} f(E)$, where $f(E) = 0$ for $E < E_{n', n}$ and $f(E) = 1$ for $E \geq E_{n', n}$. Here $E_{n', n}$ is the translational threshold energy in the excitation process, for a vibrational quantum jump from n' to n . The data of column III have been obtained by assuming $\sigma_{ex}(E, n', n) = \sigma_{n', n} f(E)$ with $f(E) = 0$ for $E < E_{n', n}$; $f(E) = [1 - (E_{n', n}/E)]$ for $E \geq E_{n', n}$. The calculated values in column IV have been obtained with $f(E) = 0$ for $E \leq E_{n', n}$ and $f(E) = \{1 - [E_{n', n} + V(R_c)]/E\}$ for $E \geq E_{n', n}$, describing the energy dependence of $\sigma_{ex}(E, n', n)$ according to equation (2)

Δn	Measured ⁽¹⁶⁾ (\AA^2)		Calculated (\AA^2)
	II	III	IV
8	0.6 ± 0.4	5 ± 3	1.4
7	7 ± 2	17 ± 5	6.3
6	4.3 ± 1.5	23 ± 7	9.6
5	5.3 ± 2	45 ± 20	12.4
4	12 ± 10	66 ± 50	14.2
3	12 ± 10	—	15.5

dependencies (see Table 2). Krause's results, together with the calculated $\bar{\sigma}_{\Delta n}$ -values based on our quenching model and the Fisher-distribution, are given in Table 2. The value of $V(R_c)$ is small compared to $E_{n'n}$ in all cases, except for $E_{n'n} = 0$. Therefore, the E -dependence of σ_{ex} as used by us [see equations (8) and (9)], corresponds best with that assumed by Krause for column 3 of Table 2. The experimental $\bar{\sigma}_{\Delta n}$ -values have been normalized to the experimental value of $\eta(2600)$. As the experimental η -value exceeds our calculated η -value by about a factor 2 at $T_{N_2} = 2600$ K, we have to multiply our calculated $\bar{\sigma}_{\Delta n}$, as given in Table 2, by the same factor, for a correct comparison with experimental $\bar{\sigma}_{\Delta n}$ -values. Then our $\bar{\sigma}_{\Delta n}$ -results are fully consistent with those of Krause as given in column 3.

This comparison of $\bar{\sigma}_{\Delta n}$ -values provides additional evidence in favor of a non-resonant $q(n, n')$ -distribution, similar to Fisher's calculations.

Due to the small mass of H_2 , internal and translational energy distributions in a Na- H_2 beam experiment are described by approximately the same temperature (see above). Therefore similar calculations for Na- H_2 excitation, as done for Na- N_2 , are less meaningful.

Calculations of the $K(4^2P_{3/2})$ - N_2 excitation rate constants and comparison with KALFF'S⁽¹⁷⁾ crossed-beam results support the conclusions we have drawn for Na- N_2 .

6. RESONANCE EFFECTS IN ELECTRONIC-VIBRATIONAL ENERGY TRANSFER

The question of resonance effects in vibrational-electronic energy transfer during alkali-diatomic quenching collisions has attracted considerable attention in the past.^(5,20-22) Our conclusion of section 5 in favor of a non-resonant mechanism is supported by the following data:

(a) Following Refs. (21) and (22) we plotted quenching cross sections for the first resonance doublets of the alkalis for several diatomic molecules against the absolute magnitude of the energy defect, ΔE . This resonance defect is defined as the energy difference between the atomic excitation level and the nearest vibrational level of the quenching molecule.

When the doublet states were not separated in the experiments, we took the smallest ΔE -value. Results are shown in Figs. 8-10. In cases where energy transfer to the nearest vibrational level is an endothermic process (open circles), the σ_{qu} -values must be multiplied by the appropriate Boltzmann factor (> 1) to account approximately for an activation factor equal to ΔE . When the atomic level lies approximately midway between two successive vibrational levels, only the value of ΔE corresponding to the exothermic quenching process was plotted. In the calculation of ΔE , we assumed for simplicity all molecules to be in the $n = 0$ state.^(21,22) No overall systematic dependence of σ_{qu} on ΔE can be observed in Figs. 8, 9, and 10. Especially for the chemically equivalent species, H_2 , D_2 and HD, no clear-cut effect is found.

(b) BÄSTLEIN *et al.*⁽²³⁾ have measured σ_{qu} for Na(3^2P) for two N_2 -isotopes. The values of ΔE for $^{14}N_2$ and $^{15}N_2$ are +0.156 eV and +0.035 eV, respectively. In spite of this considerable difference in ΔE , σ_{qu} was found to be $(30 \pm 4) \text{ \AA}^2$ for both isotopes.

(c) TSUCHIYA and SUZUKI⁽²⁴⁾ have measured excitation-rates of Na(3^2P) in collisions with N_2 and CO behind shock waves. They could obtain relative cross sections corresponding to specified vibrational quantum jumps. They have found qualitative agreement with the non-resonant FISHER-distribution^(8,9) for both molecules.

(d) Measured vibrational relaxation times for N_2 appeared to be much smaller in a rapid expansion, when the gas is being cooled, than behind shock waves where the gas is being heated. These relaxation times were inferred from Na-line-reversal measurements,

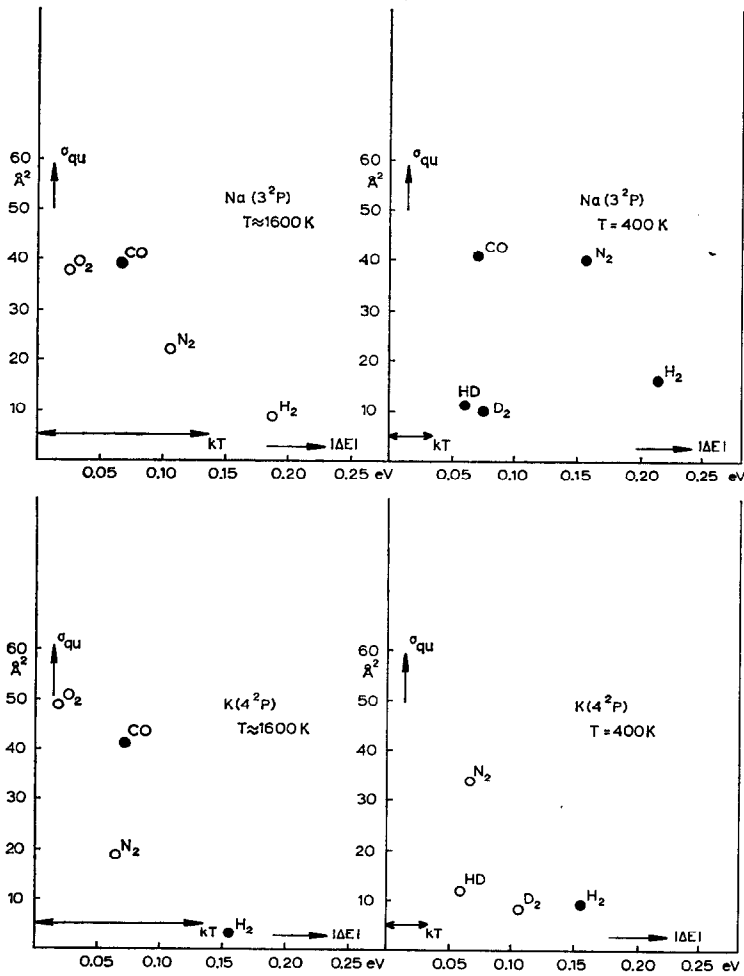


Fig. 8. Quenching cross sections for Na(3²P)- and K(4²P)-doublets at about 1600K and 400K, plotted as a function of energy defect $|\Delta E|$. Open circles denote endothermic quenching, whereas exothermic quenching is identified by closed circles. For a proper comparison, the σ -values of the endothermic processes should be multiplied by the appropriate Boltzmann factor to correct for this endothermicity. The value of kT is given by the appropriate arrows in the figures. As an example, for $\Delta E = 0.1$ eV, the corresponding Boltzmann factor is about 20 at $T = 400$ K and about 2 at $T = 1600$ K.

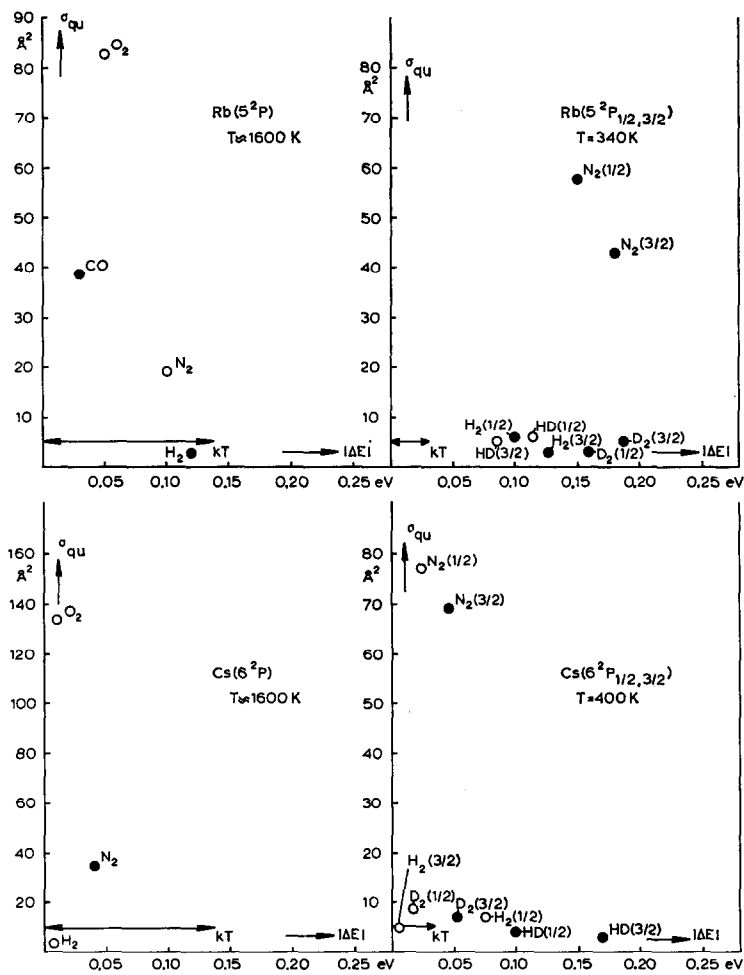


Fig. 9. As in Fig. 8, but for the Rb(5^2P)- and Cs(6^2P)-doublets. Cross sections measured for separate doublet levels are denoted by addition of the appropriate j -value in brackets.

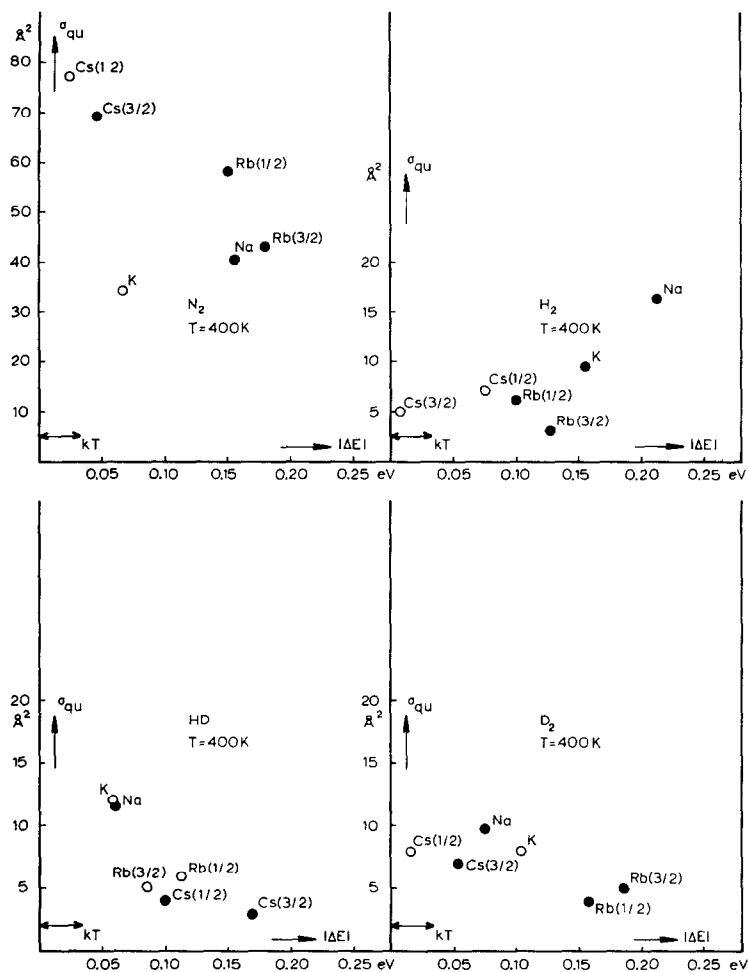


Fig. 10. Quenching cross sections for the first resonance doublets of Na, K, Rb and Cs for N_2 , H_2 , HD, and D_2 plotted as a function of the energy-defect $|\Delta E|$ at 400K.

analyzed on the basis of resonant Na- N_2 electronic-vibrational energy transfer. MACDONALD⁽²⁵⁾ has shown that the existing discrepancy in relaxation times can be fully removed by re-analyzing the same experiments on the basis of a non-resonant FISHER-distribution^(8,9).

(e) SADOWSKI *et al.*⁽²⁶⁾ measured Na-excitation by vibrationally hot N_2 in a flowing afterglow system. They found evidence in support of a strongly resonant Na- N_2 energy transfer. However, their analysis was based on a previous interpretation of KRAUSE's beam experiment, which has been re-analyzed in Ref. (16). More recently, DUGAN and SADOWSKI⁽²⁷⁾ have observed Na-emission line profiles, again in a flowing N_2 -afterglow. They then concluded that vibrational energy transfer need not be as tightly matched to the excitation energy as suggested in Ref. (26).

7. CONCLUSIONS

The temperature dependence of alkali-N₂ quenching cross sections can be explained semi-quantitatively by the simple theoretical model based on an ionic intermediate state, if we take into account van-der-Waals forces on the initial potential energy curve. From comparisons of quenching and excitation experiments, it may be concluded that the relative distribution of cross sections for specified vibrational transitions in the quenching process is described qualitatively by the theory of FISHER and SMITH.^(8,9) A distribution calculated by BJERRE^(18,19) can be definitely rejected. From our comparison of quenching and excitation experiments and from a survey of the available literature, we obtained conclusive evidence for the non-resonant character of vibrational-electronic energy transfer in alkali-N₂ quenching and excitation collisions.

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