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Excitation of Sodium Atoms by Collisions with Vibrationally Excited Molecules behind Shock Waves

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Simultaneous measurements of Na D and CO fundamental emissions have been made behind a shock wave in CO–Ar or CO–N_2–Ar mixture containing a trace of Na vapor. The relaxation of a population in each vibrational level is calculated by use of Montroll-Shuler equation. The Na D emission intensity behind the shock wave in the 1.5% CO+Ar mixture nearly follows the relaxation of CO molecules excited to a vibrational level $v=3$ or 4, which is energetically lower than the 3^2P state of Na. This means that most Na atoms are excited by collisions with CO molecules in a level higher than $v=3$, and that the Na D reversal temperature exceeds the vibrational temperature of CO molecules behind the shock wave. In contrast to this, excitation of Na behind the shock wave in the 1.7% CO+49.3% N_2+49.0% Ar mixture is due to collisions with N_2 molecules in a level higher than $v=6$, and a nearly resonant vibrational-to-electronic energy transfer is realized. The relative values of the exciting rate k_v^e by collisions with CO or N_2 in a level v are determined to be $k_1^e : k_2^e : k_3^e : k_4^e : k_5^e = <0.01 : 0.04 : 1 : 1.6 : <2$ for Na–CO and $k_4^e : k_5^e : k_6^e : k_7^e : k_8^e = <0.03 : 0.21 : 1 : 1.4 : <2$ for Na–N_2 collisions at about 2600°K.

It is well known that the collision cross-section of an inert monoatomic gas for quenching the Na D fluorescence is very small or zero, while those of molecular gases are of the same order of magnitude as the gas kinetic ones. This is one of the evidences of the efficient energy transfer from the electronic to vibrational modes of molecules and the very poor coupling between the electronic and translational motions. Gaydon and Hurle[1,2] proposed that the Na D reversal temperature behind a shock wave in N_2 or other molecular gases was the same as the vibrational temperature of molecules, and they determined the vibrational relaxation times of some diatomic gases from the profiles of Na D reversal temperature behind shock waves. This means that Na atoms are excited by collisions with molecules in a vibrational level nearly resonant to the 3^2P state of Na. Other results in line with the above idea have been reported on the electronic excitation of Na atoms by collisions with vibrationally excited N_2 molecules in an electrical discharge[3] and in thermal beams.[4] However, these experiments could not give direct information on a vibrational state of N_2 whose energy was transferred to the electronic state of Na. To clarify this point, two experiments concerning the quenching process of excited atoms were carried out. Polanyi and coworkers observed the infrared emission induced in CO[5] and NO[6] through the quenching of Hg(6^3P), and concluded that less than half of the electronic energy was transferred to vibrations of CO and NO. Burrow and Davidovits[7] examined the vibrational state of N_2 which quenched Rb(5^2P) by the superelastic electron impact method, and found the vibrational state of a certain quantity of N_2 to be $v=5$ which was

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[1] A. G. Gaydon and I. R. Hurle, Eighth Symposium (International) on Combustion, Williams & Wilkins (1962), p. 309.

[2] I. R. Hurle, *J. Chem. Phys.*, **41**, 3911 (1964).

[3] W. L. Starr, *ibid.*, **43**, 73 (1965).

[4] J. E. Mentall, H. F. Krause, and W. L. Fite, *Discuss. Faraday Soc.*, **44**, 157 (1967).

[5] G. Karl, P. Kruus, and J. C. Polanyi, *J. Chem. Phys.*, **46**, 224 (1967).

[6] G. Karl, P. Kruus, J. C. Polanyi, and I. W. M. Smith, *ibid.*, **46**, 244 (1967).

[7] P. D. Burrow and P. Davidovits, *Phys. Rev. Lett.*, **21**, 1789 (1968).

nearly resonant to the 5^2P state.

In this work, we have measured the emissions of CO fundamental and Na D line at the same position behind shock waves in CO–Ar and CO–N_2–Ar mixtures containing a trace of Na vapor, and found a correlation between vibrational relaxation and electronic relaxation. The purpose of this experiment is to examine whether the electronic excitation temperature of Na is the same as the vibrational temperature or not, and to determine vibrational levels of diatomic molecules that can excite Na atoms most efficiently.

Experimental

The shock tube used is a stainless steel pipe of 10 cm i.d. with the test section of 460 cm and the driver section of 100 cm in length. The test section was evacuated to less than 10^{-4} Torr, and the leak rate was about 10^{-2} Torr/hr. Mylar film was used as a diaphragm which was ruptured spontaneously by the accumulating pressure of H_2 gas. Three windows are placed 400 cm away from the diaphragm; two quartz windows for measurement of the Na D doublet lines and calibration of a glass prism monochromator by passing a light beam across the tube from an appropriate light source, and the other CaF_2 window perpendicular to the light path of Na D line for the infrared emission. An infrared filter (Optical Coating Lab., LO-04260) and an Au-doped Ge detector (Philco, GPC-201A) were used to isolate and detect the CO fundamental emission. The time constant of the detector and an amplifier system was about 2 μsec. The Na D doublet was measured by a monochromator with a photomultiplier 1P21. The shock velocity was determined by two Pt film gauges placed 30 cm in front of and behind the observation windows.

The sample gases Ar, N_2, and CO were commercially available ones, and their nominal purities were 99.99% for Ar, 99.98% for N_2, and 99.5% for CO. The CO gas was purified by successive distillation using molecular sieve 5A at liquid nitrogen temperatare, and other gases were introduced into a mixing tank through a trap cooled by liquid nitrogen. A trace of Na vapor was added to the sample gas as fine dust by feeding the gas into the shock tube through a trap filled with Na vapor at 10^{-2}—10^{-3} Torr. By this method, a roughly controlled quantity of Na vapor could be mixed in the shock-heated gas, and the time required for colloidal Na to vaporize was very short. This was ascertained by measurement of the absorption of Na D line. No Na D emission was observed in a shock-heated gas without introduction of Na vapor by the above procedure.

Results

Figure 1(a) shows an example of emission profiles of CO fundamental and Na D line behind a shock wave in the 1.5% CO+Ar mixture. The intensity of CO fundamental increases exponentially with a time lapse after the shock arrival, and that of Na D line rises gradually toward its equilibrium value. The latter phenomenon is explained by the fact that Na atoms are excited by collisions with vibrationally excited CO molecules. Previously,[8] we ascertained that the collision cross-section of Ar atom for quenching Na(3^2P) was less than 10^{-3}Å^2. A similar conclusion for a Cs-(6^2P)–He collision was reported by Dodd, Enemark, and Gallagher.[9] Thus, Ar atoms have no role in the excitation of Na atoms in a shock-heated CO–Ar mixture.

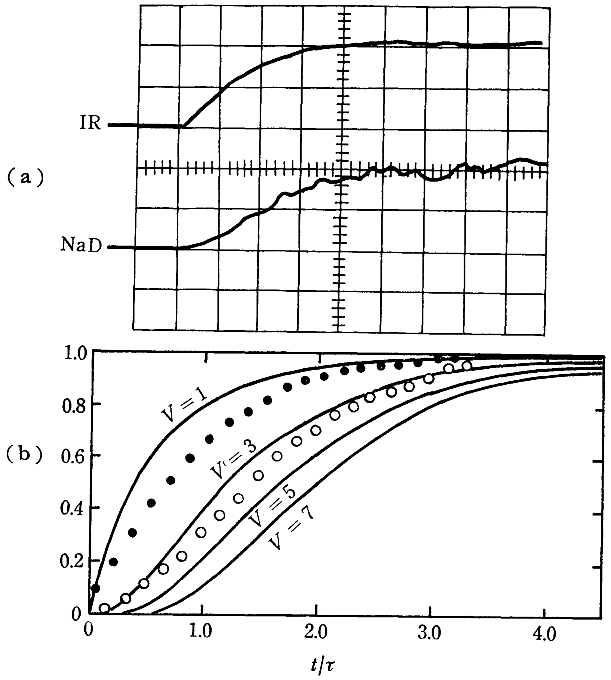

Fig. 1. (a) Emission profiles of CO fundamental and Na D line behind a shock wave in the 1.5% CO+Ar mixture.

(b) Vibrational relaxation of CO molecules in level v calculated from the above result and the excitation relaxation of Na atoms. Shock condition: $U_s=1.63$ mm/μsec, $p_2=518$ Torr, $T_2=2620$°K, $p_2\tau=$ 74.0 atm.μsec, and sweep velocity=20 μsec/division. ♯332.

— $\frac{x_v(t)}{x_v(\infty)}$, ● $\frac{I_{\mathrm{CO}}(t)}{I_{\mathrm{CO}}(\infty)}$, ○ $\frac{I_{\mathrm{Na}}(t)}{I_{\mathrm{Na}}(\infty)}$

The vibrational relaxation of CO in the CO–Ar mixture can be followed by the CO fundamental emission. Here, we make three assumptions: (1) the vibration of CO is harmonic, (2) only single quantum transitions are possible, and (3) the transition probability from $v=i$ to $v=i-1$ and that from $v=i$ to $v=i+1$ obey the relations, $P(i;-1)=iP(1;\ -1)$ and $P(i;+1)=(i+1)P(1;+1)$. For this case, Montroll and Shuler[10] showed that the vibrational distribution in each level was of the Boltzmann type, and the vibrational temperature T_v could be defined throughout the relaxation process. Thus, the concentration of CO in the v-th vibrational level should be given by

$$x_v = M(1-\mathrm{e}^{-\Theta})\mathrm{e}^{-\Theta}, \tag{1}$$

where $\Theta=hc\omega/kT_v$ (ω=vibrational frequency in cm^{-1}) and M is the total concentration of CO, *i.e.*, $M=\sum_v x_v$. The relaxation of the vibrational energy $E(T_v)$ is formulated to be

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[8] S. Tsuchiya and K. Kuratani, *Combustion and Flame*, **8**, 299 (1964).

[9] J. N. Dodd, E. Enemark, and A. Gallagher, *J. Chem. Phys.*, **50**, 4838 (1969).

[10] E. W. Montroll and K. E. Shuler, *ibid.*, **26**, 454 (1957).

$$1 - E(T_v)/E(T) = \mathrm{e}^{-t/\tau}, \qquad (2)$$

where $E(T)$ is the vibrational energy in equilibrium with the translational temperature T and τ the vibrational relaxation time. Since the vibrational energy is proportional to the intensity of the fundamental vibration, the relaxation time is determined experimentally by use of Eq. (2), and the vibrational temperature during the course of the relaxation can be expressed as a function of t/τ considering the relation $E(T_v) = \boldsymbol{M}\boldsymbol{h}\boldsymbol{c}\omega\mathrm{e}^{-\Theta}/(1-\mathrm{e}^{-\Theta})$. The concentration in each vibrational level during the relaxation can then be calculated as shown in Fig. 1(b). Applicability of the Montroll-Shuler equation to the present problem will be discussed later.

The Na D emission intensity can be assumed as a thermal emission under optically thick conditions, since the concentration of Na atoms is about 10^{11}—10^{12} atoms/cc, which is estimated from absorption measurement. Hence, the imprisonment of the Na D resonance line is effective for the present system, and the intensity is given by

$$I_{\mathrm{Na}} = E_{\mathrm{D}} B^{\circ}(\omega_{\mathrm{D}}, T_{\mathrm{exc}})\overline{\Delta\omega}\cdot\Delta\Omega\cdot\Delta s, \qquad (3)$$

where B° is a steradiancy from the black body at a temperature T_{exc}, ω_{D} the wavenumber of Na D line, $\overline{\Delta\omega}$ a spectral slit width of the monochromator, $\Delta\Omega$ a solid angle of a light flux incident on the monochromator, Δs an area of the slit, and E_{D} an effective emissivity defined by

$$E_{\mathrm{D}} = \int g(\omega', \omega_{\mathrm{D}})\{1 - \exp[-k(\omega')L]\}\mathrm{d}\omega' \Big/ \int g(\omega', \omega_{\mathrm{D}})\mathrm{d}\omega', \qquad (4)$$

where $g(\omega',\omega_{\mathrm{D}})$ is a slit function of the monochromator set at the wavenumber of ω_{D}, $k(\omega)$ absorption coefficient, and L the optical depth of gaseous emitter. The emissivity depends only on the concentration of Na atoms, and is assumed to be constant in the flowing gas behind a shock wave. Therefore, the ratio of the intensity at time t to that at an equilibrium region far from a shock front is

$$\begin{aligned} I_{\mathrm{Na}}(t)/I_{\mathrm{Na}}(\infty) &= B^{\circ}(\omega_{\mathrm{D}}, T_{\mathrm{exc}})/B^{\circ}(\omega_{\mathrm{D}}, T_2) \\ &= \exp[-(\boldsymbol{h}\boldsymbol{c}\omega_{\mathrm{D}}/\boldsymbol{k})(1/T_{\mathrm{exc}} - 1/T_2)] \\ &= [\mathrm{Na}^*]_t/[\mathrm{Na}^*]_\infty, \qquad (5) \end{aligned}$$

where T_2 is the translational temperature behind a shock wave, and Na* denotes Na(3^2P) atom. Thus, the relative concentration of Na(3^2P) or the excitation temperature T_{exc} can be obtained from the Na D emission measurement.

The energy exchange process between the electronic and vibrational states of Na and CO is represented by

$$\mathrm{Na} + \mathrm{CO}(v) \rightleftarrows \mathrm{Na}^* + \mathrm{CO}(v-\Delta), \qquad (6)$$

where the vibrational quanta Δ of CO is transferred to or from the electronic state of Na, and the exciting and quencing rates are denoted by $k^e{}_{v,\Delta}$ and $k^q{}_{v-\Delta,\Delta}$. The quenching process occurs efficiently in every gas kinetic collision, and the exciting probability is very large in a collision with a CO molecule in a particular vibrational level. Thus, the quasi-equilibrium between the electronic and vibrational states of Na and CO can be assumed, *viz.*, the relation,

$$[\mathrm{Na}^*]/[\mathrm{Na}] = (\sum_v k_v{}^e x_v)/[(\sum_v k_v{}^q x_v) + k_r], \qquad (7)$$

holds during the relaxation process behind a shock wave. In this equation

$$k_v{}^e = \sum_{0\leq\Delta\leq v} k^e{}_{v,\Delta} \text{ and } k_v{}^q = \sum_{0\leq\Delta\leq v^*} k^q{}_{v,\Delta},$$

where v^* is the nearly resonant level to the 3^2P state of Na; $v=8$ for CO and $v=7$ or 8 for N_2, and k_r is a rate of radiative loss. In the present experimental condition, the radiative loss of Na(3^2P) can be neglected as shown previously,[8] and the denominator on the right-hand side of Eq. (7) is close to $k_0{}^q x_0 + k_1{}^q x_1$, which is nearly constant throughout the relaxation process. Reasons for this are: (1) a very poor population in a vibrational level higher than $v=2$ in the temperature range of the present experiment, and (2) it is reasonable to assume that the quenching rate of molecules in the vibrationally ground state does not differ from that of first excited molecules (Ref. 17 and Discussion). The emission intensity relative to that at the equilibrium region far after the shock arrival is then represented by

$$\begin{aligned} I_{\mathrm{Na}}(t)/I_{\mathrm{Na}}(\infty) &= \sum_v k_v{}^e x_v(t)/\sum_v k_v{}^e x_v(\infty) \\ &= \text{const.} \sum_v k_v{}^e[\mathrm{e}^{-v\Theta}(1-\mathrm{e}^{-\Theta})], \qquad (8) \end{aligned}$$

and the relative values of $k_v{}^e$'s can be estimated by comparing the profile of I_{Na} with the calculated ones of x_v's.

It is seen from Fig. 1(b) that the experimental plots of $I_{\mathrm{Na}}(\mathrm{t})/I_{\mathrm{Na}}(\infty)$ nearly agree with those of $x_v(t)/x_v(\infty)$ when $v=3$ or 4. This seems that Na atoms are excited mainly by collisions with CO molecules in the vibrational level $v=3$ or 4, *i.e.*, the contribution of terms with $v=3$ or 4 to the right-hand side of Eq. (8) is very large as compared with that of a term with another v. Hence, the relative values of $k_v{}^e$'s may be calculated by the least square method using the equation

$$\begin{aligned} y(\equiv I_{\mathrm{Na}}(t)/I_{\mathrm{Na}}(\infty)(1-\chi)^{-1}) &= \sum_v k_v{}'\chi^v \\ &\approx k_2{}'\chi^2 + k_3{}'\chi^3 + k_4{}'\chi^4, \end{aligned}$$

where $\chi = \mathrm{e}^{-\Theta}$ and $k_v{}' = \text{const. } k_v{}^e$. The calculation was made by using observed values of y and χ at an interval of 0.1 of t/τ in the range that $t/\tau=0.3$—3.0. The maximum value of $k_1{}'$ was estimated by the assumption that $y = k_1{}'\chi$ when $t/\tau=0$—0.3, and that of $k_5{}'$ by the equation

$$\sum[y - (k_2{}'\chi^2 + k_3{}'\chi^3 + k_4{}'\chi^4) = k_5{}'\sum\chi^5,$$

where the notation $\sum$ means to sum up the experimental values at an interval of 0.1 of t/τ. In order to ascertain the reliability of the result obtained by the above method, the same procedure was applied to a case of contribution from other vibrational states, *e.g.*, $v=1$, 2, and 3 or $v=4$, 5, and 6. However, the result was physically untenable, since the conditions $k_v{}^e \geqq 0$ and $k_v{}^e \geqq k_{v-1}{}^e$ were not satisfied. The relative values of $k_v{}^e$'s thus calculated are summarized in Table 1, from which we can conclude that most Na atoms are excited by collilions with CO molecules in a level higher than $v=3$. The experimental accuracy of Na D emission intensity is not enough to determine the

Table 1. Relative value of the exciting rate k_v^e of Na atoms in Na–CO collisions behind shock waves in the 1.5% CO + Ar mixture

Exp. no.	U_s mm/μsec	p_2 Torr	T_2 °K	$p_2\tau$ atm. μsec	k_1^e	k_2^e	k_3^e	k_4^e	k_5^e	k_6^e
332	1.63	518	2620	74.0	<0.01	0.09	1	1.9	<2.4	—
348	1.66	522	2710	59.7	<0.01	0.05	1	1.3	<1.8	—
368	1.67	502	2730	58.9	—	<0.02	1	3.3	4.3	< 6
381	1.815	469	3190	41.7	<0.09	0.3	1	1.4	<1.7	—
387	1.48	667	2220	194	<0.09	0.5	1	3.0	<4.5	—
363	1.54	570	2370	133	<0.07	0.3	1	3.7	<7.3	—
				mean^a)	<0.01	0.04	1	1.6	<2.0	—

a) Mean values of k_v^e's are calculated by the least square method using the former three data, nos. 332, 348, and 368, with the assumption $T_2=2690$°K.

Table 2. Relative value of the exciting rate k_v^e of Na atoms in Na–N_2 collisions behind shock waves in the 1.7% CO+49.3% N_2+49.0% Ar mixture

Exp. no.	U_s mm/μsec	p_2 Torr	T_2 °K	$p_2\tau$ atm. μsec	k_3^e	k_4^e	k_5^e	k_6^e	k_7^e	k_8^e
240	1.945	427	2540	138	<0.01	0.03	0.3	1	<3.0	—
242	1.96	418	2580	133	<0.03	0.09	0.2	1	<2.5	—
244	1.96	415	2570	126	—	<0.04	0.08	1	3.7	< 5
				mean^a)	—	<0.03	0.2	1	1.4	< 2

a) Mean values of k_v^e's are calculated by the least square method using all the data with the assumption $T_2=2560$°K.

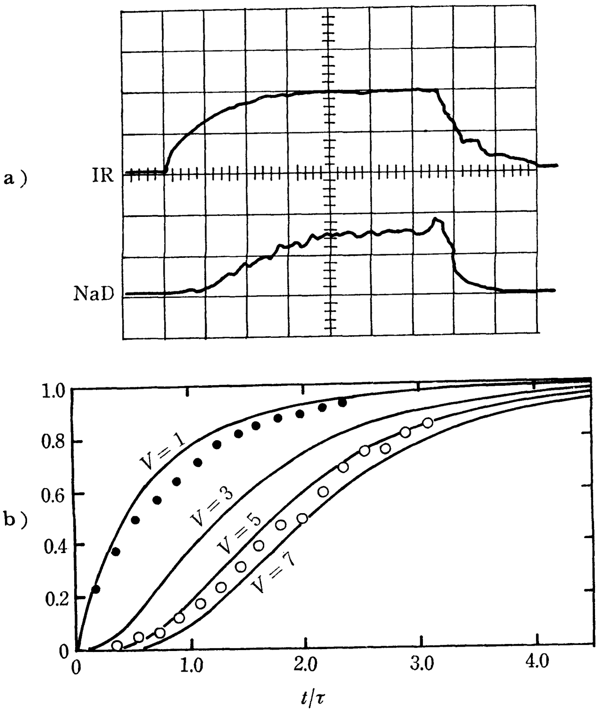

Fig. 2. (a) Emission profiles of CO fundamental and Na D line behind a shock wave in the 1.7% CO+49.3% N_2+49.0% Ar mixture.

(b) Vibrational relaxation of N_2 molecules in level v calculated from the above result and the excitation relaxation of Na atoms. Shock condition: $U_s=1.945$ mm/μsec, $p_2=427$ Torr, $T_2=2540$°K, $p_2\tau=138$ atm. μsec, and sweep velocity=50 μsec/division. #240.

— $\frac{x_v(t)}{x_v(\infty)}$, ● $\frac{I_{CO}(t)}{I_{CO}(\infty)}$, ○ $\frac{I_{Na}(t)}{I_{Na}(\infty)}$,

relative values of k_v^e's more than three, and the error is large for k_v^e at high vibrational levels owing to poor population.

The observed emission profiles of Na D and CO fundamental behind a shock wave in the 1.7% CO+49.3% N_2+49.0% Ar mixture are shown in Fig. 2(a). In a previous paper,[11] we proposed the vibrational relaxation equation for a diatomic gas mixture, and obtained the collision probability of the vibration-vibration energy exchange between CO and N_2. According to the result, the vibrational relaxation of CO should closely follow that of N_2. Since the concentration of CO is much smaller than that of N_2, and the collision cross-sections of CO and N_2 for quenching Na(3^2P) are of a similar magnitude,[12] the exciting or quenching collisions of CO molecules with Na atoms scarcely contribute to the whole intensity of Na D line. Analysis for the determination of relative values of k_v^e's is the same as that for the case of CO. As seen from Fig. 2(b), the excitation of Na atoms is made mainly by collisions with N_2 molecules in vibrational levels $v=5$—7. The calculated results are shown in Table 2. A nearly resonant vibrational-to-electronic energy transfer between N_2 and Na can be concluded. This is in line with Gaydon and Hurle's postulate.[1]

Discussion

The relaxation of the population in each vibrational level has been calculated by use of the Montroll-Shuler equation, based on the foregoing three assumptions.

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11) Y. Sato, S. Tsuchiya, and K. Kuratani, *J. Chem. Phys.*, **50**, 1911 (1969).

12) D. R. Jenkins, *Proc. Roy. Soc.* (London), **A303**, 453 (1968).

Appropriateness of this procedure should be discussed. The vibrational excitation of CO in a CO–Ar mixture proceeds by two processes (this is the same for a N_2–Ar mixture). One is a gain or loss of vibrational quanta Δ by collision with Ar or CO through the translation-vibration (T-V) energy transfer

$$\text{(i)}\quad \mathrm{CO}(i) + \mathrm{M} \rightleftarrows \mathrm{CO}(i+\Delta) + \mathrm{M}.$$

The other is a resonant or near-resonant vibration-vibration (V-V) energy transfer process

$$\text{(ii)}\quad \mathrm{CO}(i) + \mathrm{CO}(j) \rightleftarrows \mathrm{CO}(i+\Delta) + \mathrm{CO}(j-\Delta).$$

According to this mechanism, the relaxation of population x_i in the i-th vibrational level is given by

$$\begin{aligned} \mathrm{d}x_i/\mathrm{d}t = Z\sum_{\Delta\geq 1}\{[&P(i-\Delta;\ \Delta)x_{i-\Delta} + P(i+\Delta;-\Delta)x_{i+\Delta}] \\ &- [P(i;\ -\Delta) + P(i;\ \Delta)]x_i\}N \\ + Z\sum_{j}\sum_{\Delta\geq 1}\{[&Q(i-\Delta, j; \Delta)x_{i-\Delta}x_j + Q(i+\Delta, j; -\Delta)x_{i+\Delta}x_j] \\ &- [Q(i, j; -\Delta) + Q(i, j; \Delta)]x_ix_j\}, \end{aligned} \tag{9}$$

where Z is the collision frequency, N the concentration of whole particles CO and Ar, and the probabilities for the forward processes of (i) and (ii) are represented respectively by $P(i;\ \Delta)=\phi_A P_A(i;\ \Delta)+\phi_{CO}P_{CO}(i;\ \Delta)$ and $Q(i,j;\ \Delta)$, in which ϕ_A and ϕ_{CO} are mole fractions of Ar and CO, and P_A and P_{CO} are the corresponding T-V probabilities by collisions with Ar and CO, respectively. Since $Q \gg P$, a quasi-equilibrium in the distribution of population in each vibrational level can be assumed during the relaxation process as proposed by Treanor, Rich, and Rhem.[13] That is, the vibrational relaxation proceeds keeping the second term in Eq. (9) equal to zero.

If we can assume that a CO molecule is a harmonic oscillator, the quasi-equilibrium condition results in the Boltzmann distribution, and the vibrational temperature can be defined. Then, Eq. (9) is reduced to

$$\begin{aligned} \mathrm{d}x_i/\mathrm{d}t = ZN\sum_{\Delta\geq 1}[&P(i;\ -\Delta)(\rho^\Delta x_{i-\Delta} - x_i) \\ &- P(i+\Delta;\ -\Delta)(\rho^\Delta x_i - x_{i+\Delta})], \end{aligned} \tag{10}$$

where $\rho=\exp(-\boldsymbol{hc}\omega/\boldsymbol{k}T)$ and $P(i-\Delta;\ \Delta)=\rho^\Delta P(i;\ -\Delta)$ from the detailed balancing. Here, we will take a first momentum $V=\sum_i ix_i$ from Eq. (10). The result is

$$\mathrm{d}V/\mathrm{d}t = ZN\sum_{\Delta\geq 1}\Delta\sum_i P(i+\Delta;\ -\Delta)(\rho^\Delta x_i - x_{i+\Delta}). \tag{11}$$

By assuming the Landau-Teller rule of transitions,

$$\begin{aligned} P(i+\Delta;\ -\Delta) = (1/\Delta!)&(i+1)(i+2) \\ &\ldots\ldots(i+\Delta)P(\Delta;\ -\Delta), \end{aligned} \tag{12}$$

Eq. (11) can be written as

$$\begin{aligned} \mathrm{d}V/\mathrm{d}t = ZNM\sum_{\Delta\geq 1}&\Delta P(\Delta;\ -\ \Delta)\{\rho^\Delta[1 + (V/M)]^\Delta \\ &- (V/M)^\Delta\}, \end{aligned} \tag{13}$$

where $M=\sum_i x_i$. If the quantity, $X=1-E/E(T)$ is defined to represent the departure of vibrational energy E from $E(T)$ in equilibrium with translational temperature T, the relaxation of vibrational energy can be written as

$$\begin{aligned} -\mathrm{d}X/\mathrm{d}t = ZN\sum_{\Delta\geq 1}&\Delta(\rho/1-\rho)^{\Delta-1}P(\Delta;\ -\ \Delta)[(1-\rho X)^\Delta \\ &- (1-X)^\Delta], \end{aligned} \tag{14}$$

where the relations $M=E(T)(1-\rho)/\rho\boldsymbol{hc}\omega$ and $V=E(T_v)/\boldsymbol{hc}\omega$ are used to derive the above equation from Eq. (13). This shows that the multiple quanta transitions cause non-linearity in the relaxation equation, and that the relaxation cannot be described as a simple exponential approach toward the equilibrium state. If all the terms higher than X in Eq. (14) are neglected, the equation should be similar to that of Landau-Teller, and an apparent relaxation time τ can be defined as

$$1/\tau = ZN\sum_{\Delta\geq 1}\Delta^2\rho^{\Delta-1}/(1-\rho)^{\Delta-2}P(\Delta;\ -\Delta). \tag{15}$$

In Fig. 3, the exact calculation for the system, where both the single and double quanta transitions contribute to relaxation, is compared with the above approximate solution, and the diference between the relaxing vibrational energies in both models is only 10% even if $P(2;\ -2)/P(1;\ -1)=0.1$. Therefore, to apply the Landau-Teller relaxation equation to the experimental analysis means to automatically take into account to a certain extent the contribution from multiple quanta transitions.

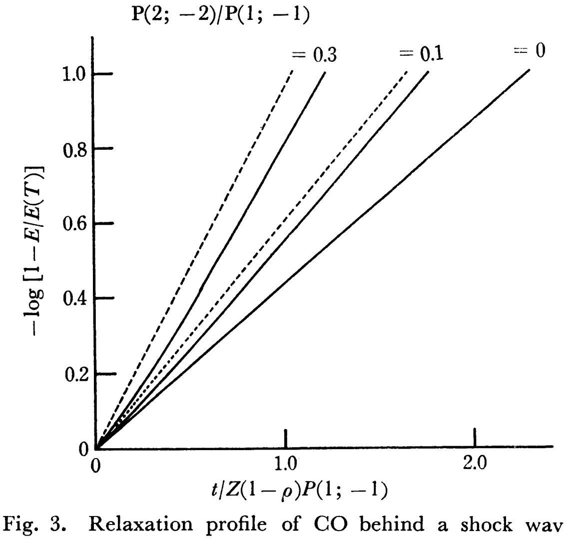

Fig. 3. Relaxation profile of CO behind a shock wave of 2000°K with single and double quanta transitions.
Solid line: exact solution, dotted line: approximate solution neglecting X^2 term.

It is probable that the real vibrational relaxation deviates from that of the Landau-Teller-Montroll-Shuler equation due to anharmonicity, especially for molecules in a high vibrational level. The quasi-equilibrium condition for a system of anharmonic oscillators results in a non-Boltzmann distribution.[13] In the shock-tube experiment, the translational temperature is higher than the vibrational one, though the latter cannot be uniquely defined. For this case, an effective vibrational temperature $\theta_v{}^*$ for a vibrational level v is lower than $\theta_1{}^*$ for the level $v=1$. Calculation of $\theta_v{}^*/\theta_1{}^*$ as a function of $\theta_1{}^*/T$ shows that $\theta_v{}^*/\theta_1{}^*$ is 0.97 for CO in a level $v=8$ when $\theta_1{}^*/T=0.3$. This value of $\theta_v{}^*/\theta_1{}^*$ is for the initial stage of the relaxation where the population of highly excited molecules which contribute to the excitation of Na is very small.

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[13] C. E. Treanor, C. W. Rich, and R. G. Rhem, *J. Chem. Phys.*, **48**, 1798 (1968).

TABLE 3. RELATIVE VALUES OF THE EXCITING AND QUENCHING RATES k_Δ^e AND k_Δ^q OF Na ATOM IN Na–CO AND Na–N_2 COLLISIONS AT ABOUT 2600°K

vib. quanta transferred, Δ		1	2	3	4	5	6	7	8
Na–CO	k_Δ^e	<0.01	0.04	1	0.6	<0.4	—	—	—
	k_Δ^q	<0.1	0.1	1	0.2	<0.04	—	—	—
	k_Δ^q (calcd)[a]	0	0.72	1	1.3	0.94	0.34	0.16	0.03
Na–N_2	k_Δ^e	—	—	—	<0.04	0.3	1	0.5	<0.8
	k_Δ^q	—	—	—	<0.5	1.0	1	0.1	<0.06
	k_Δ^q (calcd)[a]	0	0.35	0.62	0.97	1.30	1	0.32	0

a) Relative values of k_Δ^q (calcd) at 0.1 and 0.2 eV of initial kinetic energies for Na–N_2 and Na–CO collisions, repectively, are those calculated by Bauer *et al.*[17]

Thus, a large deviation from the Boltzmann distribution cannot be expected in the present experimental condition. The remaining effects of the anharmonicity are the enhancement of the multiple quanta transitions and the difference in values of $\exp(-E_v/\boldsymbol{k}T_v)$ (E_v is a real energy level) and $\exp(-v\boldsymbol{hc}\omega/\boldsymbol{k}T_v)$. The former can be rejected from the preceding discussion, and the latter effect causes little change in curves of $x_v(t)/x_v(\infty)$ in Figs. 1 and 2. The absolute values of x_v must be corrected by a factor $\exp[(v\boldsymbol{hc}\omega-E_v)/\boldsymbol{k}T_v]$, which does not produce a serious effect on the present conclusion.

The uncertainty in the population distribution can be eliminated by a direct measurement of the vibrational relaxation of highly excited molecules, especially in a level energetically near the 3^2P state. Lack of this experiment is the weakest point in this kind of work. However, we can say at least that the excitation temperature of Na atoms does not agree strictly with the the vibrational temperature of CO, while it nearly agrees with that of N_2 if the molecules are assumed to undergo relaxation of the Landau-Teller type.

The detailed balancing equation for process (6) is

$$k^e_{v,\Delta}/k^q_{v-\Delta,\Delta} = (g^*/g)\exp[-(E^* - \Delta\boldsymbol{hc}\omega)/\boldsymbol{k}T], \tag{16}$$

where g is the degeneracy of Na(3^2S), g^* the combined degeneracies of the two 3^2P states, E^* the electronic energy of Na(3^2P), and T a translational or rotational temperature. If it is possible to suppose that the exciting or quenching rate is only dependent on the vibrational quanta Δ transferred to or from the electronic state of Na and independent of vibrational states of colliding molecules, the exciting rate $k_\Delta{}^e$ and consequently the quenching rate $k_\Delta{}^q$ can be estimated as shown in Table 3. This means that the energy transfers of vibrational quanta $\Delta=3$—4 in Na–CO collisions and $\Delta=5$—6 in Na–N_2 collisions are most effective. Thus, about half of the electronic energy must be supplied from the translational or rotational motion to excite Na(3^2S) by collision with CO.

The relation between the excitation temperature of Na and the vibrational temperature of molecules may be discussed by Eqs. (7) and (16). Equation (7) can be simplified by the aforementioned assumption that $k^e{}_{v,\Delta}=k_\Delta{}^e$and $k^q{}_{v,\Delta}=k_\Delta{}^q$ for all v, and is written as

$$[\text{Na}^*]/[\text{Na}] = \sum_{0\leq\Delta\leq v^*} k_\Delta{}^e \exp(-\Delta\boldsymbol{hc}\omega/\boldsymbol{k}T_v)/\sum_{0\leq\Delta\leq v^*} k_\Delta{}^q,$$

where the radiative process is neglected. Combining the above equation with the equation of detailed balancing Eq. (16), the following relation can be derived.

$$\exp(-E^*/\boldsymbol{k}T_{\text{exc}}) = \sum_{0\leq\Delta\leq v^*} k_\Delta{}^q \exp[-(E^*/\boldsymbol{k}T) + (\Delta\boldsymbol{hc}\omega/\boldsymbol{k})(1/T - 1/T_v)]/\sum_{0\leq\Delta\leq v^*} k_\Delta{}^q. \tag{17}$$

In a thermal equilibrium system in which $T=T_v$, Eq. (17) shows that $T_{\text{exc}}=T$, while $T_{\text{exc}}\neq T$ in the system of $T\neq T_v$. For the latter, the relation of T_{exc} to T_v can be clarified by assuming that only the vibrational energy of $\Delta^*\boldsymbol{hc}\omega$ is exchanged with the electronic state of Na, where Δ^* means the most effective vibrational quanta transferred in the vibrational-to-electronic energy transfer, that is, $k_{\Delta q}=0$ when $\Delta\neq\Delta^*$. Then, we have

$$1/T_{\text{exc}} = (\Delta^*\boldsymbol{hc}\omega/E^*)/T_v + [1 - (\Delta^*\boldsymbol{hc}\omega/E^*)]/T. \tag{18}$$

In the case of resonant vibrational-to-electronic energy transfer, we get

$$\Delta^* = v^*,\ T_{\text{exc}} = T_v.$$

On the other hand, in a non-resonant case, $\Delta^*<v^*$, we obtain

$$T < T_{\text{exc}} < T_v \quad \text{or} \quad T > T_{\text{exc}} > T_v.$$

The vibrational relaxation time obtained by measuring the Na D emission behind a shock wave in CO should be shorter than that determined from the CO fundamental emission, since $T_{\text{exc}}>T_v$. Figure 4(a) represents the relaxation of the vibrational energy calculated from the emission profiles of CO fundamental and Na D emissions, for which the assumption $T_v=T_{\text{exc}}$ is made. The vibrational energy defined by the Na excitation is nearer to its equilibrium value than the real energy observed by the infrared emission. This may be referred to the fact that the main contribution to the excitation of Na is caused from CO molecules in a level $v=3$ or 4. However, an apparent relaxation time which is determined from a slope of linear plots, $\log(1-E/E(T))$ *vs.* t, does not differ so much from the true one. The difference between the two slopes is less than 10%, which is of a magnitude comparable to an experimental error of the Na D emission measurement. Thus, vibrational relaxation times in CO or CO–Ar mixture observed by separate measurements of the Na D and CO fundamental emissions appear to agree with each other as Russo has found.[14] The same analysis for a CO–N_2–Ar mixture is shown in Fig. 4(b), and the vibrational relaxations measured by both methods agree quite well. This indicates the resonant mechanism in the vibrational-to-electronic energy transfer, and is in line with Hurle's experiment.[2)]

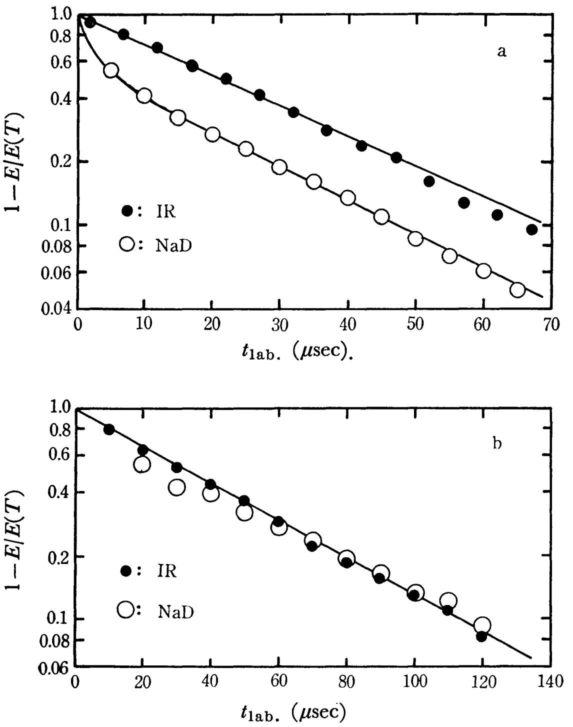

Fig. 4. (a) Relaxation of the vibrational energy of CO behind a shock wave in the 1.5% CO+Ar mixture.
(b) Relaxation of the vibrational energy of N_2 behind a shock wave in the 1.7% CO+49.3% N_2 +49.0% Ar mixture. Two values of $E/E(T)$ are determined from infrared emission measurement, $I_{CO}(t)/I_{CO}(\infty)$, and from the NaD emission by assuming that $T_v=T_{exc}$.

Russo[14)] also observed the vibrational relaxation in the expanding flow of the 5%CO+Ar mixture by measuring the Na D reversal and CO vibrational temperatures, and found that the ratio of the relaxation time τ_e to that of the shock-wave experiment τ_s is 10^{-2}—10^{-3} for the infrared method, and 10^{-1}—10^{-2} for the Na D method. Since $T_v > T$ in the expanding flow and $\Delta^* = 3$—4, T_{exc} must be lower than T_v if a non-Boltzmann distribution is not taken into account. This suggests a smaller value of τ_e/τ_s for the Na D method than that for the infrared method, while a non-Boltzmann distribution caused by the V-V coupling of anharmonic oscillators has a reverse effect. However, it seems impossible to explain the difference in values of τ_e/τ_s observed by two methods in terms of the latter effect. A later experiment by Rosenberg, Taylor, and Teare[15)] shows that H atoms as an impurity reduce considerably the relaxation time of CO in the expanding flow. Hence, the Na excitation temperature observed by Russo might be abnormally high by the chemi-excitation mechanism $H+H+Na \rightarrow H_2+Na^*$.

Theoretical calculation for the quenching process, $Na(3^2P)+N_2(0) \rightarrow Na(3^2S)+N_2(v)$, was made by Bjerre and Nikitin[16)] and by Bauer, Fisher, and Gilmore.[17)] They proposed that the adiabatic potentials of $Na(3^2P)+N_2(^1\Sigma_g^+)$ and $Na(3^2S)+N_2(^1\Sigma_g^+)$ were crossed by the surface $Na^+ + N_2^-$, and that the non-adiabatic transitions occurred at these crossing points. This model explains well the large quenching cross-section of N_2, though the collision process without crossing or approaching of initial and final potential surfaces results in a very small cross-section.[18)] Bjerre and Nikitin calculated the classical trajectories on the potential surfaces by applying the Landau-Zener formula to the transitions at crossing points, and obtained the final classical vibrational energies of N_2 and quenching probabilities. Their result shows the vibrational states of N_2 molecules, to which the energy of $Na(3^2P)$ is transferred, to be mostly in $v=1$—4. This is incompatible with our results. Bauer *et al.* treated the process in terms of a diffusion of the probability flux through a two-dimensional network of potential curves characterized by the electronic and the vibrational states of N_2 and N_2^-. The transition probability at each crossing point is given by the Landau-Zener formula, in which the transition matrix element is the product of an electronic interaction function and a Franck-Condon factor between the vibrational states of N_2 and N_2^-. In Table 3, their results are compared with ours in order to show qualitative agreement.

Conclusion

The excitation of Na atoms to the 3^2P state behind the shock wave in a CO–Ar mixture follows the vibrational excitation of CO molecules to levels $v=3$—4 rather than to a level $v=8$ which is energetically resonant to the 3^2P state of Na. The result is derived with the assumption that the vibrational relaxation of CO proceeds under the condition of Landau-Teller. Analysis of this result shows that most Na atoms are excited by collisions with CO molecules in a vibrational level higher than $v=3$, and the remaining energy to excite Na atoms is supplied from the translational or rotational motion of the colliding atom and molecule. In contrast to this, the excitation of Na atoms is made by collisions with vibrationally excited N_2 molecules in levels $v=5$—7, and the process is a nearly resonant vibrational-to-electronic energy transfer. Thus, the Na excitation temperature behind the shock wave in a N_2–Ar mixture is nearly in agreement with the vibrational temperature of N_2. The results are compatible with the theoretical calculation based on the mechanism that a Na atom is excited *via* an ionic state $Na^+ \cdots CO^-$ or $Na^+ \cdots N_2^-$ in the process of molecular collision.

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