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Theoretical Estimates of Vibrational Relaxation in Nitrogen up to 40,000 K

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Vibrational relaxation of N_2 molecules is considered at temperatures up to 40,000 K in gas mixtures that contain electrons as well as heavy collision partners. The theory of vibrational excitation due to N_2-N_2 collisions is fit to experimental data to 10,000 K by choice of the shape of the intermolecular potential and size of the collision cross section. These values are then used to extrapolate the theory to 40,000 K. Electron collisions promote vibrational transitions much more readily than the heavy particle collisions; and equilibration of vibrational temperature with the electron temperature occurs almost instantaneously for many practical purposes. Subsequently, vibrational relaxation depends on heavy particle collisions; the electrons merely drain off some of the vibrational energy changes and delay the approach to full equilibrium. As temperature increases beyond 10,000 K, multiple quantum jumps become increasingly important and small perturbation assumptions become invalid. However, these effects compensate such that small perturbation results provide a fair approximation at somewhat higher temperatures than might be expected. Anharmonic effects do not appear to be highly important to the total relaxation rate at temperatures up to 40,000 K, though they distort the transition rates in the uppermost levels.

Nomenclature

a = half-life of collision perturbation
D = energy of dissociation
E_0 = collision energy, $\mu u^2/2$
E_i = vibrational energy in level i
E_v = equilibrium vibrational energy
F_{ij} = dimensionless Fourier transform for transition i to j
f = fraction of excitation energy retained in vibration
$f(t)$ = perturbation forcing function
H_{ij} = perturbation matrix element for transition i to j
$\hbar$ = Planck constant/2π
i_m = maximum quantum level
K_{ij} = rate coefficient for excitation from state i to j
k = Boltzmann constant
L = characteristic length for collision potential
$M(n, b)$ = Kummer's function
N = density of all collision partners
n = total density of oscillators
n_i = density of oscillators in state i
P_{ij} = probability of transition from state i to j
Q_v = vibrational partition function
r = distance between colliding partners
S_0 = collision cross section
T = kinetic temperature of heavy gas particles
T_e = kinetic temperature of electrons
T_v = vibrational temperature
U = collision perturbation potential
U_0 = constant far collision perturbation
u = collision velocity
x = dimensionless collision energy $\mu u^2/2kT$; also, dimensionless oscillator coordinate $(\mu\omega^2/2D)^{1/2}y$
x_e = mole fraction of electrons
x_m = mole fraction of heavy particles
y = oscillator displacement
ϵ = energy gained by classical oscillator in units of $\hbar\omega$
θ = characteristic vibrational temperature $\hbar\omega/k$
μ = reduced mass
τ = vibrational relaxation time
τ_i^0 = relaxation for collisions with specie i at unit concentration
φ_i = vibrational wave function for state i

Introduction

THE theory of vibrational relaxation in diatomic molecules was first developed by Landau and Teller,[1] who found that the rate of collision induced vibrational relaxation varies as $\exp\{-(\theta/T)^{1/3}\}$, where θ is a characteristic temperature related to the steepness of the potential between colliding particles. Their derivation was based on purely classical arguments about the collision, but subsequent derivations by Schwartz et al.[2] based on quantum theory, and by Sharp and Rapp[3] based on semiclassical arguments, gave essentially the same results. All experimental vibrational relaxation data for diatomics have compared well with the Landau-Teller theory. For example, very good data on vibrational excitation of N_2 has been provided by Appleton[4] and by Hanson and Baganoff.[5] Figure 1 shows the comparison between their data and the theory based on the simple exponential collision potential

$$U = U_0 \exp[(y - r)/L] \tag{1}$$

where the constant U_0 establishes the size of the potential, y the displacement of the oscillator from its equilibrium position, r the distance between centers of mass of the colliding particles, and L a characteristic length that determines the potential's steepness. The data shown in Fig. 1 are values measured near the start of the vibrational excitation process; as the gas nears the equilibrium, both investigators[4,5] found that final relaxation times are decreased by a factor of two or so compared with the expected values. This effect becomes more pronounced at higher temperature.

Theories of vibrational relaxation are generally based on one-dimensional collinear collisions with harmonic oscillators having constant cross section and on small perturbation approximations. Hansen[6] shows that a three-dimensional collision model gives essentially the same result (collision cross

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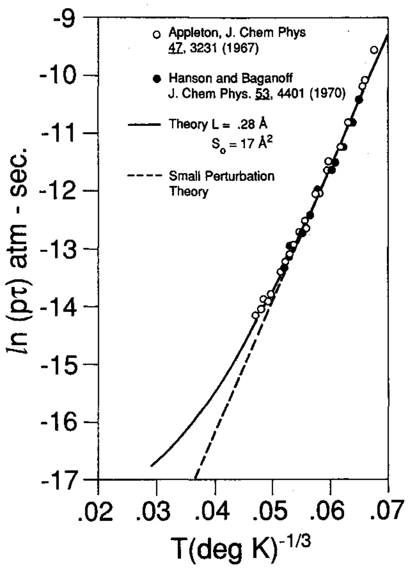

Fig. 1 Experimental and theoretical rates of vibrational relaxation in pure N_2.

section is only a weak function of collision energy) and Kerner[7] derives corrected expressions for transitions of harmonic oscillators that occur at very high energies where the small perturbation approximation breaks down and multiple quantum transitions occur. These refinements were thought to be somewhat moot in view of the fact that the simple model fits the data very well up to 10,000 K, the limit attained in experiment, whereas at higher temperatures the molecules dissociate. Although molecular states disappear in equilibrium gases at high temperature, Park[8] finds that in highly nonequilibrium flow downstream from shock waves created by hypersonic vehicles traversing the atmosphere at very high altitude, the N_2 molecules are so tightly bound that they persist significant distances in the flow. In fact, Park's computational fluid dynamic (CFD) computations indicate that vibrational relaxation of N_2 in the blunt leading regions of such vehicles may be a major factor determining the shock standoff distances from the vehicle. This in turn determines the amount of radiating gas and the total heat load to the vehicle at that locale. Thus there are now practical reasons why the theory of molecular vibrational excitation needs to be extended to higher temperatures. The purpose of this paper is to improve estimates of N_2 vibrational relaxation at temperatures up to 40,000 K by including the effects of multiple quantum transitions and of electron collisions, and making some allowances for anharmonicity that occurs in the upper vibrational levels.

Vibrational Relaxation in Pure Gas

The small perturbation theory of harmonic oscillator excitation predicts that only nearest neighbor vibrational transitions are allowed. This result leads to an exactly exponential rate of approach to vibrational equilibrium. However, it is not necessary to invoke the exponential relation; the reciprocal of the relaxation time τ at any given instant may be defined with perfect generality

$$\frac{1}{\tau} = \frac{\dot{E}_v}{E_v(T) - E_v(T_v)} \tag{2}$$

where $\dot{E}_v$ is the rate of change in vibrational energy, $E_v(T)$ the equilibrium vibrational energy at the temperature T, and $E_v(T_v)$ the vibrational energy assuming that the vibrational levels are occupied by a Boltzmann-like distribution characterized with the single temperature T_v. This assumption rests on the concept that very few collisions are needed to thermalize the vibrational states. For harmonic oscillators the denominator of Eq. (2) is

$$E_v(T) - E_v(T_v) = n\hbar\omega\left(\frac{1}{e^{\theta/T} - 1} - \frac{1}{e^{\theta/T_v} - 1}\right) \tag{3}$$

where n is the concentration of oscillators and θ is $\hbar\omega/k$, or 3395 K for N_2.

The rate of change of vibrational energy is established by the rate coefficients K_{ij} for change from vibrational state i to j. If the molecules are all in the ground state

$$\dot{E}_v = Nn\hbar\omega\sum_{i=1}^{i_m} i\left(\frac{n_i}{n}\right)K_{0i} = Nn\hbar\omega(1 - e^{-\theta/T_v}) \times \sum_{i=1}^{i_m} ie^{-i\theta/T_v}K_{0i} \tag{4a}$$

Note that the total density of collision partners N need not be the same as the density of oscillators n. The maximum number of vibrational levels i_m will be limited by the dissociation energy D. For harmonic oscillators $i_m = (D/\hbar\omega)$, about 33 for N_2.

After the gas has relaxed to the vibrational temperature T_v, the excitation and de-excitation rates from all levels are

$$\begin{aligned}\dot{E}_v &= Nn\hbar\omega\sum_{i=1}^{i_m}\sum_{j=0}^{i-1}(i-j)\left(\frac{n_j}{n}K_{ji} - \frac{n_i}{n}K_{ij}\right)\\ &= \frac{Nn\hbar\omega}{Q_v}\sum_{i=1}^{i_m}\sum_{j=0}^{i-1}(i-j)(e^{-j\theta/T_v}K_{ji} - e^{-i\theta/T_v}K_{ij})\end{aligned} \tag{4b}$$

where Q_v is the vibrational partition function. The first terms in the sum over j are the energy gains for all transitions coming to the level i from below, whereas the second terms are the energy losses for all downward transitions from the level i.

Initially i_m should be terminated below the dissociation limit since levels about kT below the limit will tend to be depleted by rapid escape to the dissociated continuum, at least until the atom concentration builds to the point where three-body recombination reactions neutralize some of the dissociation reactions. For the present, we consider the case where atom densities are far below equilibrium and the upper vibrational levels are depleted. The distribution is then truncated at $(D - kT)$ as suggested by some approximate solutions to the master equations.[6]

$$i_m = \frac{D}{\hbar\omega} - \frac{T}{\theta} \tag{5}$$

Dividing Eq. (4b) by Eq. (3) provides the reciprocal of the product $N\tau$. For harmonic oscillators

$$\frac{1}{N\tau} = \frac{1 - e^{-\theta/T_v}}{(e^{\theta/T} - 1)^{-1} - (e^{\theta/T_v} - 1)^{-1}} \times \sum_{i=1}^{i_m}\sum_{j=0}^{i-1}(i-j)(e^{-j\theta/T_v}K_{ji} - e^{-i\theta/T_v}K_{ij}) \tag{6}$$

The dimensions of $N\tau$ are molecule-s/cc or mole-s/cc, depending on the units of the rate coefficients. The pressure-relaxation time product $(p\tau)$ is the usual parameter plotted on a Landau-Teller plot as shown in Fig. 1. This is obtained by multiplying $N\tau$ by kT or RT depending on the units. Results will be presented here as the product $N\tau$ because that is the natural parameter to use when considering mixtures of different gases.

Vibrational Relaxation in Gas Mixtures

At high temperatures gases develop a number of different collision partners that have different rate coefficients for vibrational excitation; for example, molecules, atoms, and electrons. The definition of τ_i^0 is a standard relaxation time given by Eq. (6) when the oscillators are in a pure bath of species i having unit concentration. Then for the mixture

$$\frac{1}{N\tau} = \sum_i \frac{n_i/N}{\tau_i^0} = \sum_i \frac{x_i}{\tau_i^0} \tag{7}$$

where N is the total concentration of collision partners and x_i is the mole fraction of species i.

Rate coefficients for most heavy collision partners will be about the same, since they all equilibrate to the same kinetic temperature quickly, even when particle masses differ by a factor of two or so. However, different kinetic temperatures may need to be considered in nonequilibrium gases containing light species like hydrogen or helium, and often a different electron kinetic temperature T_e is required when the very lightweight electrons are present—as they are in flowfields about high speed vehicles traversing the upper atmosphere.

Vibrational Relaxation in Gas Mixtures with Electrons

Consider first a three-temperature gas in which the heavy particle temperature T, the electron temperature T_e, and the vibrational temperature T_v are all different. In a complete CFD computation of nonequilibrium flow, these temperatures and all species concentrations would be tracked using the appropriate rate equations along with conservation of energy, mass, and momentum. The vibrational relaxation time for the mixture is

$$\frac{1}{N\tau} = f\sum_i \frac{x_i}{\tau_i^0(T)} + \frac{E_v(T_e) - E_v(T_v)}{E_v(T) - E_v(T_v)}\,\frac{x_e}{\tau_e^0(T_e)} \tag{8}$$

where x_e is the mole fraction of electrons and f the fraction of the energy fed to the vibrational modes by heavy particle collisions that is not transferred to electron kinetic energy by $e + N_2$ collisions. The unit concentration standardized relaxation rate due to electron bombardment takes the same form as Eq. (6), but the function now relates to an equilibrium vibrational energy based on the electron temperature T_e. To relate all terms to the same equilibrium at the temperature T, the term expressing the electron contribution must be multiplied by the factor $[E_v(T_e) - E_v(T_v)]/[E_v(T) - E_v(T_v)]$. The rate coefficients for electron excitation of vibrations in diatomic molecules are orders of magnitude larger than for heavy particle collisions; but when T_e equals T_v, the electron collisions cause no further change in vibrational populations. In fact, it is the speed of these vibrational transitions due to electron bombardment that promotes the rapid equilibration between electron and vibrational temperatures, even though these temperatures may be far out of equilibrium with the heavy particle kinetic temperature. A relatively good approximation to the state of the gas is often obtained assuming equality between T_v and T_e. Park[8] finds that a two-temperature model of the gas produces approximately the same results in his CFD calculations as the three-temperature model and takes far less computing time.

The energy fed into vibrations by heavy particle collision is assumed to immediately shuffle to the kinetic energy of the electrons in proportion to the equilibrium energies that obtain for each specie at the temperature T_v. Then the fraction of this energy that remains in the vibrational modes is

$$\begin{aligned} f &= \frac{x_m R\theta(e^{\theta/T_v} - 1)^{-1}}{x_m R\theta(e^{\theta/T_v} - 1)^{-1} + (3/2)x_e R T_e} \\ &= \left(1 + \frac{3}{2}\,\frac{T_v}{\theta}(e^{\theta/T_v} - 1)\frac{x_e}{x_m}\right)^{-1} \end{aligned} \tag{9}$$

where x_m is the total mole fraction of the oscillators. The sum of the contributions to vibrational excitation by the heavy specie collisions is multiplied by this fraction.

Vibrational Excitation Rate Coefficients

The rate coefficients for electron excitation of N_2 have been worked out by Huo et al.[9] using reliable numerical methods of solving Schroedinger's equation to obtain the interaction potential. In principle, similar solutions can be obtained for vibrational excitation due to molecular collision, but in practice this solution is so involved that it remains unavailable at present, though the methods of computational quantum chemistry should provide these solutions eventually, as they have for many properties of small clusters of light atoms.[10] For now, rate coefficients for vibrational excitation during $N_2 + N_2$ collisions will be estimated by fitting semiclassical theory to data up to 10,000 K, deducing the form of the potential and the value of the collision cross section that provides this fit, then using these parameters to extrapolate the theory to 40,000 K.

The expressions that follow are all derived in greater detail by Hansen.[6] The rate coefficient for excitation of vibration from level i to level j can be expressed

$$K_{ij} = \frac{\bar{u}S_0}{s} e^{(i-j)\theta/2T} \int_0^\infty P_{ij}(x)xe^{-x}\,\mathrm{d}x \tag{10}$$

where $\bar{u}$ is the mean collision velocity $(8kT/\pi\mu)^{1/2}$, S_0 the cross section which has been assumed constant and removed from the integral, and s the symmetry number (1 for heteromolecular, 2 for homomolecular collisions). The term $\exp[(i - j)\theta]\exp[(i - j)\theta/2T]$ is the Arrhenius factor that provides detailed balancing at equilibrium, P_{ij} is the probability of transition, and the variable of integration x is the dimensionless collision energy $\mu u^2/2kT$.

The simple exponential interaction potential of Eq. (1) is convenient because it leads to an analytic function for the perturbation due to collinear collision[6]

$$U = E_0\,\mathrm{sech}^2(at)\exp(\mu y/m_1 L) \tag{11}$$

where a is the half-life of the collision perturbation, $u/2L$ and m_1 the mass of the end oscillator atom struck by collision. The ratio μ/m_1 is unity for a pure gas of homonuclear molecules but becomes 3/2 when atomic collision partners appear.

Whatever the potential may be, the transition probability p_{ij} can be expressed

$$p_{ij} = (E_0/\hbar\omega)^2 H_{ij}^2 F_{ij}^2 \tag{12}$$

where H_{ij} is the perturbation matrix element and F_{ij} a dimensionless Fourier transform for the collision perturbation leading to transition from state i to j. In the present approximation

$$H_{ij} = \langle\phi_j|\exp^{(\mu y/m_1 L)}|\phi_i\rangle \tag{13}$$

$$\begin{aligned} F_{ij} &= \omega_{ij}\int_{-\infty}^{\infty} \mathrm{sech}^2(at)\,e^{i\omega_{ij}t}\,\mathrm{d}t \\ &= \pi\left(\frac{\omega_{ij}}{a}\right)^2 \mathrm{csch}\left(\frac{\pi\omega_{ij}}{2a}\right) \approx 2\pi\left(\frac{\omega_{ij}}{a}\right)^2 \exp\left(-\frac{\pi\omega_{ij}}{2a}\right) \end{aligned} \tag{14}$$

where the spatial part of the wave functions are φ_i and φ_j, and ω_{ij} or $(\omega_j - \omega_i)$ is the circular frequency for the energy change of the transition.

Whereas the true potential is not strictly a simple exponential, this approximation does not matter much if the steepest part of the potential is correctly matched by the choice of L; only that part contributes much to the Fourier transform. The limitation is not in the exponential form as much as in the assumption that L is a constant for the entire range of collision energies.

For the excitation of a classical oscillator starting from rest and subject to an impulsive forcing function $f(t)$

$$f(t) = \frac{\partial U}{\partial y} = \frac{U_0}{L}\exp\left(\frac{y - r}{L}\right) \tag{15}$$

the net amount of vibrational energy excited is, in units of $\hbar\omega$

$$\epsilon = \frac{\Delta E}{\hbar\omega} = \left(\frac{E_c}{\hbar\omega}\right)\exp^{-(x_c/x)^{1/2}} \tag{16}$$

where E_c is the characteristic energy $(4\pi^2\mu\omega^2L^2)$ and x_c the dimensionless energy $E_c/2kT$. The quantity ϵ is exactly the same as the quantum transition probability P_{01} given by small perturbation theory. If one is interested only in lower temperatures, the small perturbation theory adequately accounts for all the important transitions, namely, transitions to nearest neighbors. However, for the purpose of extrapolating the theory to very high temperatures, Kerner's multiple quantum transition probabilities[7] are pertinent; these are functions of the quantity ϵ

$$P_{mn} = m!n!e^{-\epsilon}\epsilon^{m+n}\left(\sum_{k=0}^{m<n} \frac{(-1)^k\epsilon^{-k}}{k!(m-k)!(n-k)!}\right)^2 \tag{17}$$

These transition probabilities from a given initial state to all final states sum to unity as they should. They apply strictly only to harmonic oscillators, but they seem to give a reasonably good approximation for transitions of Morse oscillators as well when the transition frequencies are adjusted appropriately.

The integrands for K_{01}, K_{02}, K_{03}, and K_{04} are shown in Fig. 2 for temperatures of 6000 and 12,000 K. The integrations of Eq. (10) were performed numerically with Gaussian quadrature. At 6000 K the small perturbation result is nearly the same as for the more exact 0-1 transition, and the contributions of the 0-2 and 0-3 transitions are very small. At 12,000 K the small perturbation result seriously overestimates the probability P_{01} and the multiple transition probabilities are growing in importance. At still higher temperatures the discrepancy, of course, becomes more pronounced. However, the small perturbation theory gives good results well beyond the temperatures where the interpretation of ϵ as a probability breaks down, since the overestimate of single quantum transitions compensates for the neglect of the multiple quantum transitions. The area under the small perturbation integrand in Fig. 2 should be compared with the sum of the areas under all of the multiple step integrands when these are weighted by the number of quanta exchanged. Eventually, however, as T increases further, the relaxation rates given by the small perturbation theory become too small, and the true rates deviate upward from the linear Landau-Teller relation. A hint of this deviation appears in the data around 10,000 K as shown in Fig. 1.

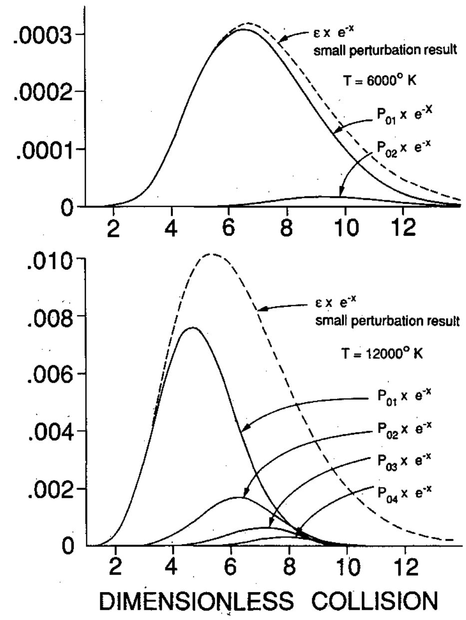

Fig. 2 Integrals used in evaluation of vibrational excitation rates of N_2 at 6000 and 12,000 K.

Table 1 Rate coefficient K_{mn} for N_2-N_2 collision excitation of vibrational level m-n rigid-rotator harmonic oscillator model

T, deg K	$\log_{10} K_{mn}$, cc/molecule-s				
$m, n =$	0, 1	0, 2	0, 3	0, 4	0, 5
5,000	−13.002	−14.649	−15.869	−16.881	−17.763
10,000	−11.391	−12.248	−12.873	−13.389	−13.840
15,000	−10.771	−11.360	−11.787	−12.139	−12.445
20,000	−10.467	−10.925	−11.255	−11.524	−11.759
25,000	−10.299	−10.681	−10.952	−11.173	−11.365
30,000	−10.202	−10.532	−10.766	−10.955	−11.118
40,000	−10.111	−10.378	−10.564	−10.713	−10.840
$m, n =$	1, 2	1, 3	1, 4	1, 5	1, 6
5,000	−12.727	−14.244	−15.388	−16.348	−17.194
10,000	−11.221	−12.012	−12.602	−13.095	−13.529
15,000	−10.688	−11.239	−11.645	−11.981	−12.277
20,000	−10.440	−10.870	−11.184	−11.443	−11.670
25,000	−10.360	−10.664	−10.923	−11.135	−11.320
30,000	−10.230	−10.539	−10.761	−10.942	−11.099
40,000	−10.159	−10.407	−10.583	−10.725	−10.847
$m, n =$	2, 3	2, 4	2, 5	2, 6	2, 7
5,000	−12.574	−14.005	−15.092	−16.013	−16.832
10,000	−11.135	−11.883	−12.445	−12.917	−13.338
15,000	−10.648	−11.171	−11.560	−11.884	−12.170
20,000	−10.428	−10.838	−11.140	−11.390	−11.609
25,000	−10.313	−10.655	−10.904	−11.109	−11.288
30,000	−10.249	−10.545	−10.758	−10.933	−11.086
40,000	−10.191	−10.429	−10.598	−10.735	−10.853
$m, n =$	3, 4	3, 5	3, 6	3, 7	3, 8
5,000	−12.470	−13.838	−14.882	−15.769	−16.567
10,000	−11.081	−11.797	−12.339	−12.795	−13.197
15,000	−10.624	−11.127	−11.502	−11.816	−12.093
20,000	−10.422	−10.818	−11.109	−11.352	−11.565
25,000	−10.319	−10.650	−10.891	−11.090	−11.265
30,000	−10.263	−10.550	−10.757	−10.927	−11.075
40,000	−10.216	−10.446	−10.610	−10.743	−10.859
$m, n =$	4, 5	4, 6	4, 7	4, 8	4, 9
5,000	−12.392	−13.711	−14.720	−15.578	−16.355
10,000	−11.042	−11.734	−12.259	−12.705	−13.098
15,000	−10.607	−11.095	−11.459	−11.765	−12.036
20,000	−10.419	−10.803	−11.087	−11.323	−11.531
25,000	−10.324	−10.647	−10.881	−11.076	−11.246
30,000	−10.274	−10.554	−10.756	−10.922	−11.067
40,000	−10.235	−10.461	−10.619	−10.751	−10.863
$m, n =$	5, 6	5, 7	5, 8	5, 9	5, 10
5,000	−12.329	−13.609	−14.591	−15.424	−16.177
10,000	−11.013	−11.686	−12.195	−12.629	−13.020
15,000	−10.596	−11.071	−11.425	−11.723	−11.988
20,000	−10.417	−10.792	−11.069	−11.300	−11.504
25,000	−10.329	−10.645	−10.874	−11.064	−11.231
30,000	−10.284	−10.559	−10.756	−10.919	−11.061
40,000	−10.251	−10.474	−10.628	−10.756	−10.869

To agree with the N_2 data it was necessary to choose the scale parameter L about 0.28×10^{-8} cm to fit the slope of the Landau-Teller plot, and the cross section S_0 about 17×10^{-16} cm^2 to match the measured values. These numbers are not very precise: although the data looks fine on a log plot, there is appreciable scatter; and the data can be fit almost equally well with values of L that differ by 10% or so, with corresponding variation in the cross sections by as much as a factor of 2. These values merely adjust whatever approximations are contained in the theory to the experiments; they are at least reasonable in view of the known size of electron wave functions and the force with which molecules repel one another when these wave functions overlap.

Some of the rate coefficients obtained using the preceding values of cross section and potential scale are given in Table 1. Rate coefficients are shown for transitions from m to $m + 5$ starting from the initial quantum state m = 0-5. These coefficients apply to a rigid rotator or to the rotational state $J = 0$. Values are shown for temperatures of 5000, 10,000, 15,000, 20,000, 25,000, 30,000, and 40,000 K.

Vibrational Relaxation of N_2 at High Temperature

With the rate coefficients K_{ij} determined, the summations of Eq. (6) were performed. Results are shown in Fig. 3. The log of $N\tau$ in units of mole-s/cc is plotted for N_2 oscillators as a function of $T^{-1/3}$. The upper curve is the unit density rate for collisions with other N_2 molecules. The lower solid curve is the unit density rate for collisions with electrons using the rate coefficients of Huo et al.[9] and of Lee.[11] These values would be used in assessing the total relaxation time of a gas mixture according to Eq. (8).

The values of $N\tau$ or $p\tau$ curve away from the linear relation at very high temperature when the correct transition probabilities are used. The relation shown in Fig. 1 is independent of vibrational temperature; the result from Eq. (4a) that applies when vibrational temperature is negligible is the same as when using Eq. (4b) that applies when the vibrational temperature is T_v. In suddenly shock heated gas relaxing toward equilibrium, the temperature T decreases as T_v increases and the sequence of calculated relaxation rates follows the Landau-Teller curve.

An important feature of the relaxation times produced by electron collisions is that they are relatively constant, the order of 3×10^{-16} mole-s/cc, no matter what the electron temperature. The rate coefficients provided by Huo et al.[9] are not quite sufficient to give convergence of the relaxation time to its final value; their tables stop at $K_{i,i+5}$, presumably because the rate coefficients are dropping precipitously as changes of six or more vibrational quanta are considered. However, these rate coefficients must be weighted by the number of quanta changed when used in the sums of Eq. (6) and the 6th and 7th level transitions still shorten the relaxation times noticeably, though higher level transitions are indeed negligible. Rate coefficients for transitions due to electron collision up to 10 quanta change have been calculated by Lee[11] with a semiempirical method. Although Lee's estimates do not exactly match the more rigorous computations, they are close enough to provide a reasonably good remainder correction that completes the convergence. Schultz[12] provides an extensive set of experimentally measured vibrational rate coefficients for $e + N_2$ bombardment. These give a slightly smaller relaxation time as shown by the dashed curve of Fig. 3, but the results are substantially the same as for the theoretical calculations.

Anharmonic Effects

The previous results have been based on harmonic oscillator models that underestimate the total number of vibrational levels and overestimate the spacing between upper levels. Consequently, a Morse oscillator has been used to evaluate some anharmonic factors that could influence vibrational relaxation at high temperature. Although the Morse potential is not as accurate as the Rydberg-Klein-Reese (RKR) potential, it is realistic enough to provide reasonable estimates of anharmonic effects that occur in real molecules. The advantage of the Morse potential is that analytic solutions for the vibrational wave functions exist so that numerical evaluation of the perturbation matrix elements is straightforward.

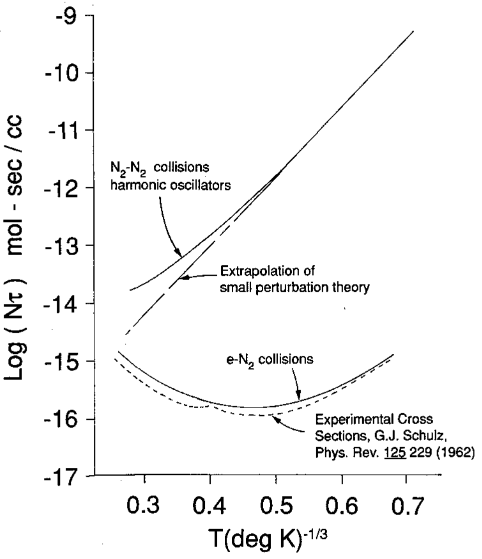

Fig. 3 Vibrational relaxation rates in N_2 due to electron collisions and to N_2-N_2 collisions.

The vibrational wave functions of a Morse oscillator are given in terms of Laguerre polynomials[13,14] or Kummer's functions. The Morse potential is

$$U/D = (1 - e^{-x})^2 \tag{18}$$

where D is the depth of the potential well and x the dimensionless oscillator coordinate given in terms of the oscillator's reduced mass μ, the vibrational frequency ω, and the displacement of the interatomic distance r from its equilibrium value r_e

$$x = (\mu\omega^2/2D)^{1/2}(r - r_e) \tag{19}$$

The wave functions for the nth vibrational level of the Morse oscillator are

$$\phi_n(z) = C_n e^{-z/2} z^{b/2} M(n, b, z) \tag{20}$$

where the coordinate z is related to the coordinate x

$$z = (4D/\hbar\omega)e^{-x} \tag{21a}$$

and the normalization constant is

$$C_n^{-2} = (b-1)![n!/(b+1)(b+2)(b+3)\cdots(b+n)] \tag{21b}$$

The coefficient b need not be an integer, but for convenience in computation is chosen as the integer nearest to

$$b \approx (4D/\hbar\omega) - 2n - 1 \tag{21c}$$

The Kummer's function $M(n, b, z)$ is

$$M(n, b, z) = 1 - \sum_{k=1}^{n} \frac{n(n-1)(n-2)\cdots(n-k+1)}{(b+1)(b+2)(b+3)\cdots(b+k)} \frac{z^k}{k!} \tag{21d}$$

The Morse oscillator potential is shown in Fig. 4, along with the wave functions for selected vibrational quantum numbers (0, 1, 3, 6, 9, and 19); these are the solid lines in Fig. 4. The dashed lines are the harmonic potential and oscillator wave functions for these same quantum levels. All of these functions are plotted against the dimensionless oscillator coordinate $(y - y_e)$ which is $(2D/\hbar\omega)^{1/2}x$. The Morse oscillator wave functions are much like the harmonic oscillator functions but merely stretched out so the same number of cycles accommodate to the wider potential, whereas the eigenvalues occur at progressively lower energy levels than the harmonic oscillator values as the vibrational quantum number increases

$$E_n = \hbar\omega[(n + 1/2) - (\hbar\omega/2D)(n + 1/2)^2] \tag{21e}$$

The matrix elements given by Eq. (13) for a linear perturbation were found to be only slightly larger for the Morse oscillator than for the harmonic oscillator. For neighboring transitions, from quantum level n to $n \pm 1$, the square of the perturbation matrix elements are related

$$\frac{H^2_{n,n\pm1}\,(\text{Morse})}{H^2_{n,n\pm1}\,(\text{harmonic})} = 1 + 0.0088(n+1) \tag{21f}$$

For a linear perturbation, the square of the harmonic oscillator matrix elements are $(n + 1)/2$ for the n to $n + 1$ transitions and $n/2$ for the n to $n - 1$ transitions. The matrix elements for multiple quantum transitions are zero or negligi-

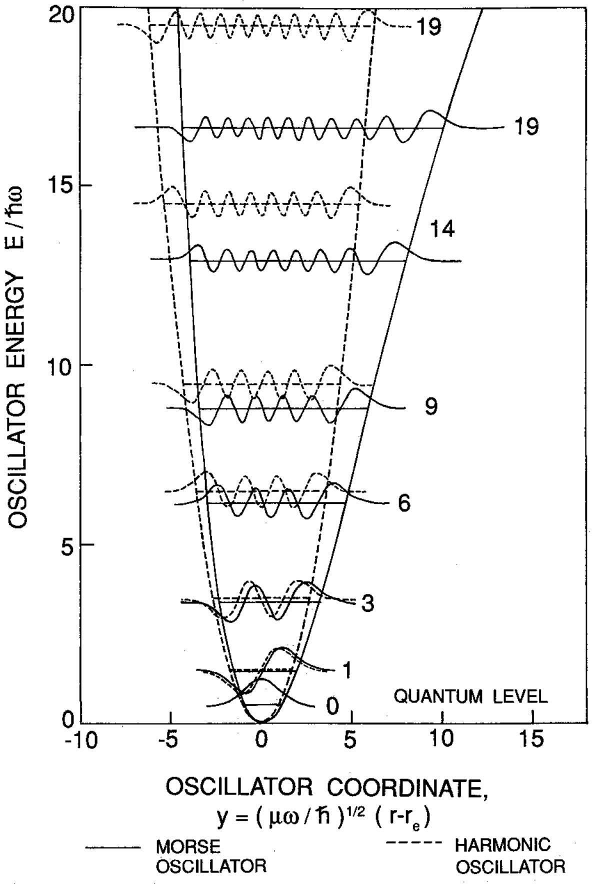

Fig. 4 Potentials and vibrational wave functions for Morse oscillators and for harmonic oscillators.

ble in either case. Multiple transitions result from a shuffling of single quantum transitions that occur during the collision event when the collision is energetic enough. This is shown in the numerical solutions to the close-coupled set of equations such as provided by Rapp and Sharp[15] and by Treanor.[16] Treanor's solutions to the close-coupled equations agree with Kerner's analytic oscillator transition probabilities for high energy collisions.

Since the perturbation matrix elements are approximately the same, the transition probabilities are primarily increased for the anharmonic oscillator by the decreased frequencies between adjacent levels, as these increase the Fourier transforms of Eq. (14). Although the transition probabilities are increased, the corresponding vibrational energy exchanges are decreased, so these effects compensate somewhat, leaving a relatively small decrease in relaxation time for the anharmonic oscillator compared with the harmonic model. The decrease in relaxation time for anharmonic oscillators in the ground rotational state is further compensated when the effect of higher rotational states is considered. As rotational quantum number increases, the oscillator potential becomes shallower with fewer vibrational eigenvalues. This effect was estimated by calculating the vibrational relaxation time for Morse oscillators having an average rotational energy $BJ(J+1) = kT$, which for N_2 occurs near $J = 100$ at 40,000 K. The effect of all of these corrections was to decrease the relaxation times for N_2 compared with the harmonic oscillator values shown in Fig. 3, but by an insignificant amount at low temperature and only about 30% at 40,000 K. When atom concentrations are less than equilibrium, the upper vibrational levels tend to be depleted by escape to the dissociation continuum in a region about kT below the dissociation limit; then the important transitions are more and more confined to the lower levels as temperature increases, and these are only mildly anharmonic. Apparently the harmonic oscillator vibrational relaxation times might serve as upper bounds which are relatively close to reality.

Concluding Remarks

In conclusion, the vibrational relaxation of N_2 is dominated by the presence of electrons only when the electron kinetic temperature is substantially different from the vibrational temperature. Once the electron and vibrational temperatures have equilibrated, the subsequent relaxation rate is established mainly by heavy particle collisions.

Small perturbation theories of heavy particle collision relaxation of vibrational energy are suspect at high temperature for a number of reasons: they overestimate the transitions to nearest neighbors, they do not account for multiple quantum changes, and they are based on harmonic oscillator approximations. However, the decrease in transition probability given by more exact theory is partly compensated by the multiple quantum jumps, so the small perturbation theory gives a useful result at higher temperatures than might be expected. The outcome is that the vibrational relaxation rate of N_2 deviates modestly from the Landau-Teller relation at 40,000 K, increasing by a factor of about three compared with the small perturbation result. The effects of anharmonicity seem to be still relatively modest at these temperatures, and the harmonic oscillator results represent a reasonably good upper bound for vibrational relaxation times. However, the small perturbation theory does noticeably underestimate the relaxation rates at high temperatures, so one may wish to account for the nonlinearity of the Landau-Teller relation when applying the theory at temperatures above 10,000 K for N_2.

The preceding conclusions are contingent on the assumption that the exponential-like steepness of the interaction potential has not changed from the value that agrees with experimental data up to 10,000 K. No doubt this question can be settled using validated methods of computational quantum chemistry.

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