EFFECTS OF H_2O VAPOR ON VIBRATIONAL RELAXATION IN EXPANDING AND CONTRACTING FLOWS

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Abstract

As opposed to previous explanations based on the effects of anharmonicity of simple diatomic molecules, traces of water vapor are suggested to be the most likely cause of the anomalously fast vibrational relaxation of such gases observed in supersonic and hypersonic nozzles. The mechanism is the strong V-VR coupling with H_2O molecules that dramatically facilitates the collisional transfer of vibrational energy. Slight moisture content is thus a real-world aspect of gas dynamics that must be considered in characterizations of shock tubes, reflected shock tunnels, and expansion tubes.

Introduction

A well-known problem in nonequilibrium diatomic gases is the greatly accelerated vibrational relaxation observed in expanding supersonic flows compared with theoretical predictions based on relaxation times deduced from shock-tube data.[1-6] Since this discrepency is impossible to explain with molecules modeled as linear harmonic oscillators (LHO's), the anharmonicity of real molecules is usually invoked to provide the rationale.

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The qualitative description of the effects of anharmonicity is very simple. As originally proposed by Treanor, Rich, and Rehm,[1] a gas expands through a sequence of vibrational population distributions given by the product of the Boltzmann ratio of number densities in the rth and ground-state levels of LHO molecules and the Treanor correction factor

$$\xi_r = \exp\left(\frac{r\vartheta_1 - \vartheta_r}{T}\right), \qquad (1)$$

where ϑ_r is a characteristic temperature defined such that $k\,\vartheta_r$ is the energy of the rth level and T is the translational temperature. Equation (1) is most easily derived by assuming that rapid, near-resonant V-V energy exchange processes enable corresponding detailed balancing on a time scale short compared with that of the drop in T. Accelerated relaxation in an expanding gas is then seen to be a two-step phenomenon: (1) V-V pumping of upper levels because the anharmonic difference $(r\,\vartheta_1 - \vartheta_r)$ in Eq. (1) increases with increasing r; (2) the operative step of enhanced V-T relaxation rate coefficients for molecules in these upper levels because of the narrower spacings between levels. The starting or stagnation temperature of the expanding flow must be at least comparable to ϑ_1 for the Boltzmann factor not to kill the participation of upper levels. None of the conditions for accelerated relaxation is met in contracting gases, as caused, for example, by the passage of a shock wave.

As compelling as the qualitative arguments for anharmonicity effects may seem, quantitatively they can account for only a small fraction of the accelerated relaxation observed in the expanding flows in reflected shock tunnels.

Calculations by Rich and Treanor,[3] and more recently by Ruffin and Park,[4] predict enhancements by at most a factor of two, whereas typical data show relaxation occurring up to two orders of magnitude faster than allowed by LHO molecules. The experimental stagnation temperatures and departures from equilibrium are not large enough for anharmonicity to do more.

Clearly, then, some additional effect is needed to explain the relaxation data. The purpose of this paper is to suggest that traces of water vapor in an otherwise pure diatomic gas may be enough to account for the differences.

Binary Mixtures

A fundamental part of any description of nonequilibrium processes is proper treatment of the tendency to approach equilibrium demanded by the second law of thermodynamics. In particular, a partial differential equation is needed to describe the behavior of the average vibrational energy e^* per molecule after a system has been knocked out of equilibrium, either by compression or by expansion. Compression deposits energy initially into the translational mode, leaving vibrational levels underpopulated relative to full equipartition of energy; expansion and cooling leave the vibrational levels relatively overpopulated. Subsequent behavior can be described mathematically by implementing the methods of reaction kinetics.
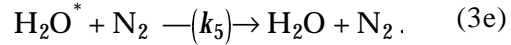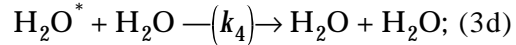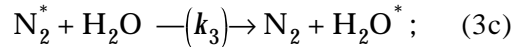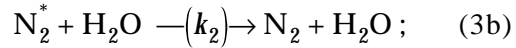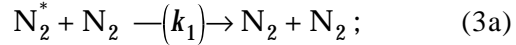
For present purposes, we assume no chemical reactions (including dissociation), no multiple quantum jumps in a molecule due to inelastic collisions, and no contributions from conventional transport processes. We also assume LHO molecules since it is effects other than anharmonicity that we are now seeking. Straightforward application of rate equations for the populations of individual vibrational levels yields the following expression for the average vibrational energy per molecule of species i:

$$\frac{De_i^*}{Dt} = \frac{1}{\tau_i}\left(e_{i,e}^* - e_i^*\right) - \sum_{j\neq i}\frac{1}{\tau_{ij}}\left(e_{j,e}^* - e_j^*\right), \quad (2)$$

where the subscript e denotes equilibrium values at the same translational temperature (introduced

through detailed balancing) and the τ's are relaxation times.

The same application of rate equations that gives Eq. (2) also gives the relaxation times in terms of rate coefficients k_i (defined herein with the units atmosphere$^{-1} \times$ second^{-1}). To be more specific, we now consider the binary mixture N_2–H_2O. Let subscripts 1 and 2 refer to N_2 and H_2O, respectively, when applied to e^*, τ, characteristic vibrational temperature ϑ, and mole fraction x. Relevant reactions are

$$N_2^* + N_2 \xrightarrow{(k_1)} N_2 + N_2 ; \qquad (3a)$$

$$N_2^* + H_2O \xrightarrow{(k_2)} N_2 + H_2O ; \qquad (3b)$$

$$N_2^* + H_2O \xrightarrow{(k_3)} N_2 + H_2O^* ; \qquad (3c)$$

$$H_2O^* + H_2O \xrightarrow{(k_4)} H_2O + H_2O; \quad (3d)$$

$$H_2O^* + N_2 \xrightarrow{(k_5)} H_2O + N_2 . \qquad (3e)$$

The rationale for the critical reaction (3c) is given in the next section.

An important feature of Eq. (2) is the last term, which couples the relaxation of species i with those of the other species and depends on the existence of exchange reactions like (3c) above. Its physical interpretation is clear: it represents impedance of the relaxation of species i by the relaxation of other species. If $e_1^* < e_{1,e}^*$ and $e_2^* < e_{2,e}^*$, for example, species 2 can increase its vibrational energy not only by V-T collisions with all molecules, but also by V-V collisions with molecules of species 1 that leave the latter with less vibrational energy and thus headed in the direction opposite from where they need to go. This particular V-V scenario and its reverse will contribute to each of $\tau_1, \tau_{12}, \tau_2,$ and τ_{21} in Eq. (2).

A point to be made here is that CFD codes treating all reactions as V-T would misrepresent the essence of N_2^* deexcitation. In particular, (3c) would be missing from the above list and the entire burden of deexcitation of N_2^* by collisions with H_2O would fall on the V-T reaction (3b). This would mean two things:

(1) a totally nonphysical value of k_2 that may have to be several orders of magnitude too large in order to compensate for the neglect of k_3; (2) a mathematical format without the explicit coupling between Eq. (2) for N_2^* and Eq. (2) for H_2O^*. Applications of such codes would be questionable.

The principal relaxation times τ_i in Eq. (2) can be written as follows for N_2-H_2O with reactions (3a)-(3e):

$$\frac{1}{p\tau_1} = \left(1 + \frac{e_{1,e}^*}{k\vartheta_1}\right)^{-1}$$

$$\cdot \left[x_1 k_1 + x_2 k_2 + x_2 k_3 \left(1 + \frac{e_2^*}{k\vartheta_2}\right)\right]; \quad (4a)$$

$$\frac{1}{p\tau_2} = \left(1 + \frac{e_{2,e}^*}{k\vartheta_2}\right)^{-1}$$

$$\cdot \left[x_1 k_3' \left(1 + \frac{e_1^*}{k\vartheta_1}\right) + x_1 k_5 + x_2 k_4\right], \quad (4b)$$

where $\quad k_3' = k_3 \exp\left(-\frac{\vartheta_1 - \vartheta_2}{T}\right) \quad$ is the rate coefficient for the backward V-V reaction. Apart from the k_3 and k_3' terms, these results are typical of combination rules usually employed in CFD codes. The strictly coupling relaxation times are

$$\frac{1}{p\tau_{12}} = \frac{x_2 k_3' \vartheta_1}{\vartheta_2}\left(1 + \frac{e_1^*}{k\vartheta_1}\right)\left(1 + \frac{e_{2,e}^*}{k\vartheta_2}\right)^{-1}; \quad (5a)$$

$$\frac{1}{p\tau_{21}} = \frac{x_1 k_3 \vartheta_2}{\vartheta_1}\left(1 + \frac{e_2^*}{k\vartheta_2}\right)\left(1 + \frac{e_{1,e}^*}{k\vartheta_1}\right)^{-1}. \quad (5b)$$

Special Properties of H_2O Molecules

Very much unlike the homonuclear N_2, water molecules have strong dipole moments to cause rapid V-T relaxation by reaction (3e), involving both dipole-quadrupole and dipole-induced dipole interactions, and especially by the self-deexcitation of (3d). Accordingly, and no matter what the relative mole fractions, the comparatively small τ_2 in Eq. (4b) enables the average excitation energy of H_2O to achieve a quasi-steady state (QSS) at each step of the much slower N_2 relaxation. More quantitatively, the QSS's must exist if the inequality

$$\frac{4}{\tau_{12}\,\tau_{21}}\left(\frac{1}{\tau_2} - \frac{1}{\tau_1}\right)^{-2} << 1 \quad (6)$$

is satisfied, which appears to be true for all N_2–H_2O mixtures and also for all O_2–H_2O mixtures. Good experimental evidence for the QSS's is provided by acoustical absorption in moist N_2.[7]

Implementation of the QSS's means $De_2^* / Dt = 0$ and thus

$$e_{2,e}^* - e_2^* = \frac{\tau_2}{\tau_{21}}\left(e_{1,e}^* - e_1^*\right) \quad (7)$$

from Eq. (2) for H_2O. Elimination of $\left(e_{2,e}^* - e_2^*\right)$ from Eq. (2) for N_2 then yields

$$\frac{De^*}{Dt} = \frac{1}{\tau}\left(e_e^* - e^*\right), \quad (8)$$

in which the subscript 1 has been dropped and the effective single relaxation time for N_2 satisfies

$$\frac{1}{\tau} = \frac{1}{\tau_1} - \frac{\tau_2}{\tau_{12}\,\tau_{21}}. \quad (9)$$

Recognition of the QSS's thereby allows the mathematical formulation of the N_2–H_2O binary mixture to be reduced to that of a single-species gas.

Water molecules have another special property that is even more important for present purposes. Their unique geometry of two light hydrogen atoms bonded roughly at a right angle between them to a far more massive oxygen atom means an unusually small moment of inertia. This, in turn, means easily induced rotational transitions and very closely spaced rotational energy levels; consequently, excellent energy matches abound between vibrational levels of most molecules and vibrational-rotational levels of H_2O. That water vapor, even in very small amounts, is observed to be a superb quencher of vibrational excitation should not be surprising.

Under most laboratory conditions, the relevant levels for the exchange reaction (3c) are the first excited vibrational state of N_2 ($\vartheta_1 = 3395$ K) and the corresponding portion of the near-continuum of rotational levels superimposed on the first excited state of the bending mode of H_2O ($\vartheta_2 = 2295$ K). Fairly crude collision modeling of this reaction, which is more aptly termed near-resonant V-VR instead of obviously nonresonant V-V, was performed by Nagel and Rogovin.[8] These authors make the key point that conventional selection rules do not apply to hard collisions, which means that significant jumps in rotational quantum numbers can and do occur in N_2–H_2O exchange collisions. They also achieved reasonable agreement with experimental data.

The bottom line is that the rate coefficient k_3 for reaction (3c) is not negligible; in particular, it is certainly orders of magnitude larger than k_1, which represents the only reaction occurring in a pure N_2 gas where vibrational relaxation is extremely slow because of the noninteractive nature of homonuclear molecules (no dipole moment). Accordingly, the comparatively few N_2^*–H_2O collisions in a slightly moist N_2 gas will be far more effective in quenching N_2 vibrational excitation that the many N_2^*–N_2 collisions. Such is the overwhelming significance of traces of water vapor in understanding nonequilibrium phenomena in laboratory test facilities.

Correction Factors for Slightly Moist Diatomic Gases

From this point on, we assume the following sequence of rate coefficients obtained from acoustical measurements[7] of moist N_2 and air and corresponding to reactions (3a)-(3e):

$$k_4 >> k_5 > k_3 > k_3^{'} >> k_1 \text{ and } k_2. \quad (10)$$

The respective values at room temperature are 10^9, 1.2×10^6, 1.2×10^5, 3.2×10^3, and 0.082 (atm.-sec.)$^{-1}$.

Though not used specifically in the brief present analysis, we also note that the rate coefficient for

$$O_2^* + H_2O \rightarrow O_2 + H_2O^*$$
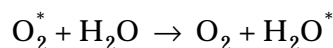
is about two orders of magnitude larger than the k_3 in Eq. (3c) because of the close match between $\vartheta(O_2) = 2239$ K and $\vartheta(H_2O) = 2295$ K. Here the near-resonance actually is V-V instead of V-VR.

Substitution into Eq. (9) of Eqs. (4a), (4b), (5a), and (5b), together with use of the inequalities in Eq. (10), gives the following approximate expression for the effective N_2 relaxation time appropriate for Eq. (8):

$$\frac{1}{p\tau} = \frac{1}{p\tau_1} \approx \left(1 + \frac{e_{1,e}^*}{k\vartheta_1} \right)^{-1}$$

$$\cdot \left[k_1 + hk_3 \left(1 + \frac{e_2^*}{k\vartheta_2} \right) \right]. \quad (11)$$

The more revealing notation $h = x_2$ to denote humidity or H_2O mole fraction has been introduced, along with $x_1 = 1 - h$.

Simple though it appears, Eq. (11) has several interesting and critical features that are worth highlighting. In the first place, only V-T self-deexcitation of N_2 and the V-VR exchange reaction of Eq. (3c) survive the cancellation of terms caused by application of Eq. (10). Secondly, since k_3 is about six orders of magnitude larger than k_1 (at least around room

temperature according to acoustical absorption data), very little water vapor is required to mask the k_1 contribution. Accordingly, it is not difficult to imagine the relaxation in most laboratory systems being controlled entirely by V-VR collisions with H_2O molecules. A third feature is the dependence of $p\tau_1$ on e_2^* as well as T, which is never possible for single-species LHO's and does not occur here unless temperatures are sufficiently high that second-order population terms are important (since the e_2^* multiplies the energy difference in Eq. (8)).

A more convenient representation is obtained by assuming the relatively instantaneous establishment of QSS Boltzmann distributions for the populations of vibrational levels of each species. This is achieved by fast, near-resonant V-V exchange reactions within species and corresponds to relaxation proceeding through a sequence of such distributions. These QSS's are also the basis for defining species vibrational temperatures according to

$$e_i^* = k\vartheta_i \left[\exp\left(\frac{\vartheta_i}{kT_{v,i}}\right) - 1 \right]^{-1}, \qquad (12)$$

with the translational temperature T replacing $T_{v,i}$ for the equilibrium energies $e_{i,e}^*$.

Unless the moist N_2 gas is extremely dilute, the existence of a vibrational temperature for N_2 seems practically assured, as does the existence of a vibrational temperature for H_2O because of the very efficient V-V transfer collisions between strong dipoles effectively compensating for the relative rarity of H_2O–H_2O collision events. On the other hand, the possibility that the two vibrational temperatures are equal to each other is somewhat remote because the interspecies V-VR collisions in reaction (3c) are not nearly as probable as the intraspecies V-V collisions involved here. The result is that current 2T CFD codes (T; $T_{v,i} = T_{v,j}$ for all i and j) may be less adequate than multiple-T codes in which each vibrational temperature is allowed to be different or perhaps not to exist at all.

In any event, for the very special gas treated in this paper and because of the aforementioned QSS for e_2^* culminating in Eq. (7), we can use

Eq. (7) again to express e_2^* in terms of parameters mostly pertaining to N_2. This procedure reintroduces some of the V-T reactions that canceled when deriving Eq. (11). The final results for small H_2O mole fraction h can be written as follows, with $T_v = T_{v,1} = T_v(N_2)$, $\vartheta_1 = \vartheta(N_2)$, and $\vartheta_2 = \vartheta(H_2O)$:

$$\frac{1}{p\tau} = gk_1 \left[1 - \exp\left(-\vartheta_1 / T\right) \right]; \qquad (13)$$

$$\frac{DT_v}{Dt} = g \left(\frac{DT_v}{Dt} \right)_{h=0}; \qquad (14)$$

$$\left(\frac{DT_v}{Dt} \right)_{h=0} = -\frac{k_1 p T_v^2}{\vartheta_1} \left[1 - \exp\left(-\vartheta_1 / T_v\right) \right]$$

$$\cdot \left\{ 1 - \exp\left[-\vartheta_1 \left(\frac{1}{T} - \frac{1}{T_v} \right) \right] \right\}, \qquad (15)$$

where the important correction factor for moisture content satisfies

$$g\left(h, T, T_v\right) = 1 + \frac{hk_3}{k_1} \left\{ 1 - \exp\left(-\frac{\vartheta_2}{T}\right) - \frac{k_3}{k_5 + hk_4} \right.$$

$$\cdot \left. \left[\frac{\exp\left(-\vartheta_1 / T_v\right) - \exp\left(-\vartheta_1 / T\right)}{1 - \exp\left(-\vartheta_1 / T_v\right)} \right] \right\}^{-1} . \qquad (16)$$

Expanding versus Contracting Flows

Clearly the dominant feature of the moisture correction factor in Eq. (16) is the factor hk_3/k_1. Although the ratio k_3/k_1 may diminish somewhat at high temperatures from its value of about 10^6 at room temperature, as determined from acoustical absorption data,[7] the message seems indisputable: traces of water vapor have the

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potential of dramatically accelerating the vibrational relaxation of otherwise pure nonequilibrium diatomic gases. Moreover, we easily understand this behavior in terms of the extremely efficient, near-resonant V-VR energy transfer collisions between N_2 molecules and H_2O molecules, as opposed to the very infrequent V-T collisions of the diatomic molecules amongst themselves. We also know that the relatively large k_3 results from the unique geometry of H_2O molecules that produces a near-continuum of rotational levels superimposed on each vibrational level to enable resonances with almost any excited diatom.

The remaining difficulty, of course, is that the potentially very large correction factor applies to contracting as well as to expanding flows. Why is it, then, that recent literature dwells almost entirely on anomalously fast relaxation in the latter? A possible answer is that this has not always been so. Even though the physics underlying the effects of water vapor was not completely understood, the importance of this impurity was recognized empirically and early-on by researchers attempting to extract relaxation times from shock-tube data. In fact, the high-temperature relaxation data base that we use today is almost exclusively that derived in the 1960's by researchers who had learned to take great care in purifying their gases. It is obvious, therefore, that huge discrepancies can result if these same relaxation times are used in comparing theoretical predictions for pure gases with data from expanding flows in reflected shock tunnels in which similar care is not taken in removing impurities. Such theory will always underestimate the relaxation rates observed in expanding flows.

Concluding Remarks

We have developed the rationale and derived simple expressions to show the remarkable effects of trace amounts of water vapor in increasing vibrational relaxation rates in nonequilibrium diatomic gases. Since such increases are predicted for both expanding and contracting flows, we have further proposed that the anomalous relaxation observed in the former may be caused by greater water content in reflected shock tunnels than in the shock tubes from which most relaxation times were deduced. This explanation is in marked contrast to the more conventional one based on the effects of anharmonicity of real molecules. Anharmonicity effects do distinguish between

expansion and contraction, but fall far short of accounting quantitatively for the differences observed.

In any event, a case is made for the importance of including impurities like H_2O in modeling flow fields in laboratory test facilities in which nonequilibrium properties and the internal states of constituent molecules play essential roles. Examples range from possible effects of molecular excitation on combustion chemistry in scramjet engines to the availability of excitation energy for conversion into flow energy in supersonic and hypersonic nozzles. Applications of the theoretical framework provided depend, of course, on the availability of an adequate set of rate coefficients as functions of temperature. These are in short supply, especially for V-V and V-VR collisions.

References

1. Treanor, C. E.; Rich, J.W.; and Rehm, R. G.: Vibrational Relaxation of Anharmonic Oscillators with Exhange Dominated Collisions. J. Chem. Phys., vol. 48, 1798-1817, 1968.

2. Bray, K. N. C.: Vibrational Relaxation of Anharmonic Oscillator Molecules: Relaxation under Isothermal Conditions. J. Phys. B (Proc. Phys. Soc., London), vol. 1, 705-717, 1968.

3. Rich, J. W.; and Treanor, C. E.: Vibrational Relaxation in Gas Dynamic Flows. Annual Review of Fluid Mechanics, vol. 2, 355-396, 1970.

4. Ruffin, S. M. and Park, C.: Vibrational Relaxation of Anharmonic Oscillators in Expanding Flows. AIAA 92-0806, Jan. 1992.

5. Cheng, H. K. and Emanuel, G. Perspective on Hypersonic Nonequilibrium Flow. AIAA Journal, vol. 33, 385-400, 1995.

6. Chiroux de Gavelle de Roany, A.; Flament, C.; Rich, J. W.; Subramaniam, V. V.; and Warren, Jr., W. R.: Strong Vibrational Nonequilibrium in Supersonic Nozzle Flows. AIAA Journal, vol. 31, 119-128, 1993.

7. Zuckerwar, A. J. and Miller, K. W.: Vibrational-Vibrational Coupling in Air at Low Humidities. J. Acoust. Soc. Am., vol. 84, 970-977. 1988.

8. Nagel, J. and Rogovin, D.: V-V Exchange Involving H_2O Molecules: A Calculation of the N_2^*–H_2O Deactivation Rate Constant. J. Chem. Phys., vol. 72, 6593-6601, 1980.