Vibrational Relaxation and Dissociation Behind Shock Waves
Part 1: Kinetic Rate Models

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This paper addresses the validation of the analytical nonperturbative semiclassical vibration-translation and vibration-vibration-translation rate models for the atom-diatomic and diatomic-diatomic vibration energy transfer molecular collisions. These forced harmonic oscillator rate models are corrected and validated by comparison with three-dimensional semiclassical trajectory calculations for nitrogen, which are widely considered to be the most reliable theoretical data available. A remarkably good agreement is shown between the two models, for both the temperature and quantum number dependence of single-quantum and double-quantum vibration-translation jumps in the temperature range 200 ≤ T ≤ 8000 K and for vibrational quantum numbers 0 ≤ ν ≤ 40. The simplicity of the theory, as well as the agreement shown, make the forced harmonic oscillator rate model attractive for master equation and direct simulation Monte Carlo modeling of nonequilibrium gas flows at very high temperatures, when the first-order, vibration-vibration-translation rate models are not applicable, and where use of the three-dimensional trajectory calculations is very cumbersome and time consuming. The forced harmonic oscillator model is also applied to obtain the probability of collision-induced dissociation of diatomics.

I. Introduction

Vibrational energy transfer in collisions of diatomic molecules plays a fundamental part in high-enthalpy gasdynamic flows, molecular gas discharges, plasma chemical reactors, and in upper atmosphere chemistry. In these environments, it creates and maintains strongly nonequilibrium molecular vibrational energy distribution functions (VDF), which induce various nonequilibrium chemical reactions, electronic excitation, dissociation, and ionization of diatomics (e.g. see Refs. 1–5). In particular, the rates of these high-energy threshold chemical kinetic processes in nonequilibrium gas flows are sensitive to the populations of the high-vibrational levels of molecules. In turn, these populations are controlled by the vibration-translation (V-T) processes

\[ AB(i) + M \rightleftharpoons AB(f) + M \]  

(1)

and vibration-vibration-translation (V-V-T) processes

\[ AB(i) + CD(t) \rightleftharpoons AB(f_1) + CD(f_2) \]  

(2)

involving highly vibrationally excited molecules. In Eqs. (1) and (2) \( AB \) and \( CD \) represent diatomic molecules, \( M \) stands for atom, and \( i, f, f_1, \) and \( f_2 \) are initial state and final state vibrational quantum numbers, respectively.

There is an extensive literature on the experimental and theoretical study of V-T and V-V-T energy transfer (see, for example, Refs. 6–12, and numerous references therein). Up to this time, experimental data for the processes (1, 2) at high-vibrational quantum numbers have been obtained only for a few heteronuclear species, such as CO and NO (see Refs. 13 and 14), and only for low temperatures, up to several hundred degrees. For homonuclear molecules such as \( \text{N}_2 \) and \( \text{O}_2 \), these data are not available. However, numerous theoretical models have been developed.6–12 One of the most popular approaches to the problem, based on the semiclassical first-order perturbation theory (FOPT), a collisional collision model and an exponential repulsive intermolecular potential, is the SSH theory.15 As is well known, FOPT more or less reliably gives only the single-jump transition probabilities \( |i - f| = 1 \) in Eq. (1) or \( |i_1 - f_1|, |i_2 - f_2|, |i_1 + i_2 - f_1 - f_2| \leq 1 \) in Eq. (2) for conditions such that the probabilities are much smaller than unity. With several or less a posteriori modifications, such as symmetrization, inclusion of anharmonicity,6–8 Van der Waals attractive forces,16 and long-range multipole-multipole forces,17 modified SSH theory is being widely used for simulation of nonequilibrium gas flows.

However, for high-collision velocities and/or vibrational quantum numbers, for which the V-V-T transition probabilities, including those for multiple quantum jumps, become large, the use of the SSH theory does not have any theoretical basis. On the other hand, attempts at "generalization" of the SSH theory for multiple jumps18,19 yield the wrong result. It has been shown that FOPT underestimates the probabilities of multiple jumps by many orders of magnitude, due to the fact that they actually occur as a sequence of single-quantum transitions (e.g., see Ref. 7 and references therein).

Among less approximate approaches we mention the exact quantum calculations, performed for the simplified collision model as used in SSH theory by Secrest and Johnson20 and the semiclassical method developed by Billing (see Ref. 9 and references therein) for three-dimensional collisions with a more realistic intermolecular potential. Trajectory calculations by the latter method have been performed for a number of species at high temperatures and high quantum numbers, including \( \text{N}_2 \) and CO. Unfortunately, the direct use of these results in modeling calculations is hardly possible due to the considerable amount of computer time that would be required.

Finally, there exists a well-known semiclassical nonperturbative analytical solution for the V-T transition probabilities of Eq. (1)
for a harmonic oscillator acted upon by an external exponential force. This is the solution that is called the forced harmonic oscillator (FHO) model. A comparison of the FHO model, developed for collinear atom-diatom collisions, with purely quantum one-dimensional calculations, showed very good agreement. The FHO approach has also been generalized by Zelechow et al. and by Skodje et al. for arbitrary V-V-T transitions in diatomic-diatomic collisions [see Eq. (2)].

Section II of the present paper discusses the possibility of using the results of the FHO theory for calculation of the V-T and V-V-T rates in diatomic gases over a wide range of collision velocities and vibrational quantum numbers, including multiple quantum jumps, and provides a validation of the FHO model by comparing its results with those of more exact models. Section III presents the conclusions and makes recommendations on rate model applications. The application of the FHO model to master equation modeling of nonequilibrium gas flows will be addressed in a separate publication.

II. Forced Harmonic Oscillator Transition Probabilities

Summarizing the results of Kermer, Treanor, and Zelechow et al., one may obtain the following expressions for the V-T transition probabilities for the process of Eq. (1) in collinear atom-diatom collisions:

\[ P(i \rightarrow f, \varepsilon) = \frac{i! f!}{e^{i f} e^{i f}} \exp(-\varepsilon) \left( \sum_{r=0}^{\infty} \frac{(-1)^r}{r!} \frac{1}{(i-r)! (f-r)!} \right)^3 \]

and for the V-V-T probabilities for the process of Eq. (2) in collinear diatomic-diatomic collisions:

\[ P(i_1, i_2 \rightarrow f_1, f_2, \varepsilon, \rho) = \sum_{r=0}^{\infty} (-1)^{i_1+i_2-r} \left( \begin{array}{c} j+1 \vspace{1mm} \hline \varepsilon \vspace{1mm} \hline \varepsilon + j+1 \end{array} \right)(C_{i_1+1, f_1+1})(C_{f_2+1, i_2+1}) \exp[-(f_1 + f_2 - r)] \]

\[ \times \left( \sum_{r=0}^{\infty} \frac{(-1)^r}{r!} \frac{1}{(i_1-r)! (i_2-r)!} \right)^2 \]

In Eq. (3), \( i \) and \( f \) are the initial and final vibrational quantum numbers of the relaxing molecule, respectively, \( n = \min(i, f) \), and \( \varepsilon \) is the average number of quanta transmitted to the initially nonvibrating oscillator (e.g., see Ref. 23). Similarly, in Eq. (4), \( i_1, i_2, i, f_1, f_2, f \), and \( \varepsilon \) are initial and final vibrational states of colliding partners, respectively, \( n = \min(i_1+i_2, f_1+f_2, f) \), and \( \varepsilon \) has the same meaning as in Eq. (3). The parameter \( \rho \) is the Massey parameter of the collision, and \( C_{ij}^{(i')} \) is the transformation matrix. The expressions for \( \varepsilon \) and \( \rho \) for a purely repulsive exponential intermolecular potential \( V(r) \sim \exp(-\alpha r) \) are as follows:

\[ \varepsilon = \frac{4\pi^2 \omega (\tilde{m}/\mu)^2 \gamma^2}{\alpha^2 \hbar} \sinh^{-1} \left( \frac{\pi \alpha \omega}{\alpha^2 \tilde{v}} \right) \]

\[ \rho = 2(\tilde{m}/\mu)\gamma^2 \alpha^2 \omega/\omega_v \]

In Eqs. (5) and (6), \( \omega \) is the oscillator frequency; \( \mu, \gamma, \mu, \tilde{m} \) are mass parameters; \( \mu = m_1 m_2/(m_1 + m_2), \gamma = m_3/(m_1 + m_2), \tilde{m} = m_{AB} m_C/(m_{AB} + m_C) \) (for diatomic-diatomic collisions \( m_{AB} = m_{AC} \)); and \( \tilde{v} \) is the collision velocity. Explicit expressions for the calculation of the transformation matrix \( C_{ij}^{(i')} \) as well as evaluations of these matrices for low \( k \) can be found in Ref. 27.

In the present paper, we use the correction of Eq. (11) rather than results of Skodje et al. for diatomic-diatomic collisions between different species, since their results have not been presented in a closed analytical form.

Unfortunately, experimental data or purely quantum calculations at high temperatures and high-vibrational level transition probabilities in diatomics are not available. Thus, to validate the use of this corrected FHO model for simulation of vibrational relaxation in diatomic gases, we compared the V-V-T rates calculated using Eqs. (3-11) with close-coupled semiclassical, three-dimensional trajectory calculations for nitrogen by Billig and Fisher, which are considered to be the most comprehensive and reliable nitrogen data available at this time. The thermally averaged V-V-T rates have been obtained from numerical integration of the probabilities (3) and (4) over a Maxwell distribution.

The steric factors for V-T and V-V rates, which are theoretically expected to be \( \frac{1}{2} \) and \( \frac{1}{2} \), respectively, have been considered as adjustable parameters. They have been obtained from matching the FHO probabilities at relatively low collision velocities:

\[ P(1, 0 \rightarrow 0, 0) \equiv S_{VT} \cdot \varepsilon \]

\[ P(1, 0 \rightarrow 0, 1) \equiv S_{VV} \cdot \rho^2/4 \]

at low \( \tilde{v} \).
to the results of Ref. 33. It has been found that both steric factors are temperature independent and equal to $S_{VT} = 4/9$ and $S_{VV} = 1/27$. Therefore, the two parameters, $\varepsilon$ and $\rho$, given by Eqs. (5) and (6) should be multiplied by $S_{VT}$ and $S_{VV}^2$, respectively. The best agreement with the data of Ref. 33 was obtained for a potential parameter $\alpha = 4.4 \text{ Å}^{-1}$.

Figure 1 shows the comparison of single-quantum V-T rates in $N_2$ calculated by the corrected FHO model, with those reported by Billing and Fisher. The behavior is quite different from that of the SSH theory, which fails both at high temperatures and at high-vibrational levels, where it predicts much higher transition probabilities (see Fig. 1). Obviously, the reason why the SSH theory overpredicts V-T rates at high-collision velocities is that the transition probabilities are of the form $P(1 \rightarrow 0) = \varepsilon \cdot \exp(-\varepsilon)$, or $P(1, 0 \rightarrow 0, 0) = \varepsilon \cdot \exp(-2\varepsilon)$, which become comparable with unity (see Fig. 2), and cannot be calculated by the SSH type first-order perturbation theory, which gives the result $P(1 \rightarrow 0)_{SSH} = \varepsilon$, exceeding unity.

The explanation of the SSH failure at high-vibrational levels (even at low temperatures) is given by Billing, based on his trajectory calculations for CO–CO and CO–He (see references in Ref. 9). He reports that to predict correctly the CO–CO V-T rate at $v \sim 30$ at $T \leq 1000$, one has to consider a large number of vibrational states coupled during the collision. Therefore, he concludes, the calculation is beyond the two-state perturbation limit, despite the fact that the resulting transition probability is small ($\leq 10^{-3}$).

Note that the observed coupling is already incorporated in the FHO theory, which takes into account all coupled states.

Another restriction on the use of SSH theory at these conditions is the influence of multiple quantum jumps, $|i - f| > 1$, which cannot be adequately described by the FOPT. The FHO approach, however, also allows calculation of these probabilities, considering multiple jumps as a series of single-quantum transitions during a single collision. Figure 3 shows the rate constants of some double V-T jumps compared to those calculated by Billing and Fisher. Again, one can see that the agreement is quite satisfactory. Figure 3 also shows that the rate constant $k_{VT}(20 \rightarrow 18)$ in nitrogen, calculated by Kume, is lower than both the Billing data and our result by 1–2 orders of magnitude.

The transition probability $P(1, 0 \rightarrow 0, 1)$, calculated using FOPT by Rapp and Englander–Golden [see Eq. (12)] has already been shown to be in very good agreement with calculations of Billing and Fisher at low and moderate temperatures $200 < T < 3000 \text{ K}$ (see Fig. 5). Figures 4 and 5 also show the temperature and quantum number dependence of the nonresonance (Fig. 4) and near-resonance (Fig. 5) single-quantum V-V rates at the higher quantum levels. One can see a satisfactory agreement between FHO model...
and Billing—Fisher results within a factor of 2–3 accuracy for the entire temperature range $200 < T < 3000$ K and for all considered transitions. The agreement shown also validates the accepted off-resonance correction of Eq. (11). Another validation of this correction is good agreement between the calculated rate of the process

$$N_2(1) + O_2(0) \rightarrow N_2(0) + O_2(1)$$

and the experimental data fit by Taylor and Bitterman$^{35}$ shown in Fig. 6. Finally, Fig. 7 presents the single- and multiquantum V-V jump rates, compared to those of Ref. 33; agreement is again satisfactory.

Note that at very high-collision velocity $\tilde{v}$ the V-V rates given by the FHO theory also substantially deviate from the SSH theory predictions (see Fig. 8). For example, using Eqs. (3) and (4), one may show that at the high $\tilde{v}$, $P(1, 0 \rightarrow 0, 1) \rightarrow \tilde{v}^2 \exp(-2\tilde{v}) = [P(1, 0)]^2$ [compare to Eq. (12)], which shows that at high-collision velocity the V-V exchange occurs as two independent V-T jumps. This results in a large spike in the transition probability $P(1, 0 \rightarrow 0, 1)$ at $\tilde{v} \geq 6$ km/s (see Fig. 8). Although the factorization of the V-V-T probabilities,

$$P(i, j \rightarrow k, l) = P(i \rightarrow k) \cdot P(j \rightarrow l)$$

as first suggested by Meador et al.$^{39}$ only approximately holds for many possible transitions even at high $\tilde{v}$, our calculations show that it does give an order-of-magnitude estimate of the V-V-T rates at $T \geq 10$ K. At the lower temperatures the use of Eq. (14) leads to a underestimation of the V-V-T probabilities by several orders of magnitude.

We conclude that the analytical FHO theory, with the corrections just mentioned, correlates well with the three-dimensional semi-classical trajectory calculations for nitrogen over a wide range of temperatures and vibrational quantum numbers, including single- and double-quantum V-T and V-V processes. The effects of non-collinear collisions and vibration-rotation coupling, taken into account in Ref. 33, are not, apparently, major influences for a heavy molecule such as $N_2$, whereas multistate vibrational coupling during the collision is a major factor. The influence of Van der Waals attractive forces, important only at low temperatures, may be also incorporated in the FHO model. This has been done by Heldrich et al.$^{35}$ who generalized the FHO model for the intermolecular Morse potential.

The effect of the long-range attractive forces, which strongly influences the V-V probabilities for CO–CO and CO–$N_2$ at low temperatures (see Refs. 37 and 38), has not been considered in the FHO model. This model, also, cannot reliably predict probabilities for V-V-T relaxation for molecular collisions involving nonadiabatic electronic transitions, as presumably occur in NO–NO collisions (see Ref. 39). However, the influence of both of these effects should dramatically decrease with temperature, and at very high tempera-
turers behind strong shock waves the FHO theory may be also applied for calculation of V-V-T transition probabilities even in these gases.

Finally, we note that the FHO theory, with the modifications discussed, may be used for obtaining state-specific rates for dissociation and bimolecular reactions. The probability of dissociation from vibrational level $i$

$$AB(i) + M \rightleftharpoons A + B + M$$

(15)

can be represented as the product of the probability of multiquantum V-T or V-V-T transition to the highest vibrational level of the molecule $v_{\text{trans}}$, and the probability of the subsequent decay, of the energetic complex,

$$P_{\text{trans}}(i \rightarrow \varepsilon) = P_{\text{VT}}(i \rightarrow v_{\text{trans}}, \varepsilon) \cdot P_{\text{decay}}(16)$$

where $P_{\text{decay}} \sim 1$. This assumption is not justified at very high $i$, when the total energy of colliding partners may greatly exceed the dissociation energy of the molecule, and the formation of the intermediate quasissbound state is unlikely. Nevertheless, for conditions where the dissociation primarily occurs from the lowest vibrational levels, which is known to happen at the region immediately behind the shock wave, where $T_r \sim T_r \gg T_r$ (see Ref. 40), Eq. (16) should give a realistic dissociation rate.

For bimolecular reactions, such as

$$AB(v) + C \rightleftharpoons AC(v') + B$$

(17)

the calculation of the state-specific rate $P(v \rightarrow v')$ requires the solution of the scattering problem for the forced harmonic oscillator with a time-dependent frequency. This solution, although not in a closed form, was obtained by Bal' et al.11 However, in the assumption of the abrupt frequency change $\omega_{AB} \rightarrow \omega_{AC}$, if the relative frequency change of the oscillator is small, this solution may be expanded using a small parameter $\delta = (\Delta \omega/2\omega)^2$ (see Ref. 41 for details). For the cases of practical interest, such as Zel'dovich mechanism reactions,

$$N_2(v) + O \rightleftharpoons NO(v') + N$$

$$O_2(v) + N \rightleftharpoons NO(v') + O$$

(18)

\[ \delta \sim 10^{-2}, \] and one can still use the FHO theory for obtaining the state-specific rates.

## III. Summary

In the present paper, we have analyzed the nonperturbative semiclassical V-T and V-V-T rate models for the atom-diatom and diatom-diatom collisions, suggested for the forced harmonic oscillator (FHO) by Kerner,21 Treanor,22 and Zelchow et al.27 The two models are corrected for three-dimensional collisions, anharmonicity of the oscillator, and for collisions between two different diatomic species. The FHO V-V-T rate model is validated by comparison with the three-dimensional semiclassical trajectory calculations by Billing and Fisher33 for nitrogen. Remarkably good agreement is shown, both for the temperature and quantum number dependence of single-quantom and double-quatom jumps in the temperature range 200 $\lesssim T \lesssim$ 8000 K and for the vibrational quantum numbers $0 \leq v \leq 40$. The FHO model is also applied for collision-induced two-step molecular dissociation.

The FHO model gives new insight into vibrational relaxation kinetics at high temperatures and may be used for master equation and direct simulation Monte Carlo modeling, as has been recently discussed in Ref. 42, of vibrationally nonequilibrium, chemically reacting gas flows behind strong shock waves, at the conditions when first-order perturbation theory (SSH theory) is known to be not applicable. Finally, the modified FHO rates as developed here are analytic and can be far more conveniently incorporated in flow calculations than can rates given by three-dimensional close-coupled numerical calculations.

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