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Existence of the Bottleneck in Vibrational Relaxation of Diatomic Molecules

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High-temperature vibrational relaxation of diatomic molecules is analyzed using master equation and Fokker–Planck diffusion equation modeling. Both approaches are based on the nonperturbative forced harmonic oscillator vibrational energy transfer rate model. The results show that the effect of the retarded diffusion at the intermediate vibrational energies during the relaxation process (bottleneck), predicted in the previous studies, does not exist at the high temperatures. It is also shown that the interpretation of the high-temperature vibrational relaxation as a diffusion-type process is inadequate because of the strong effect of multiquantum energy transfer. The obtained results, applied to interpretation of the rates of thermal dissociation, suggest an important role of rotations in molecular activation at the high vibrational energies.

I. Introduction

THIS paper addresses the nature and conditions of existence of the so-called bottleneck effect in the vibrational relaxation of diatomic molecules.[1,2] Theoretical calculations of vibrational energy transfer rates in high-temperature nitrogen at $T = 4000$ K, based on the generalized Schwartz–Slawsky–Herzfeld (SSH) theory,[1] predict a profound minimum in the rate of molecular relaxation as a function of vibrational quantum number v.[2] For example, Fig. 1 shows behavior of the second moment of vibrational transition rate coefficients $M(v)$

$$M(v) = \frac{1}{2}\sum_{w}(v - w)^2 \cdot K(v, w) \tag{1}$$

where $K(v, w)$ is the effective rate of the molecule relaxation from vibrational level v to level w (Ref. 2):

$$K(v, w) = \sum_{v',w'} f_{v'} \cdot k(v, v' \rightarrow w, w') \tag{2}$$

In Eqs. (1) and (2), v, w, v', and w' are vibrational quantum numbers, $f_{v'}$ is the relative population of vibrational level v', and $k(v, v' \rightarrow w, w')$ are individual transition rates, calculated in Ref. 1. One can see a well-pronounced minimum in $M(v)$ at vibrational energy that corresponds $v \cong 25$. The transition moment $M(v)$ given by Eq. (1) is interpreted as a diffusion coefficient in vibrational energy space.[2] Therefore, the predicted minimum (bottleneck) at the intermediate vibrational energies (about one-half of the molecular dissociation energy) would mean slowing down the vibrational quanta flow toward the high levels during the relaxation process. This would also substantially decrease the molecular dissociation rate for the conditions when dissociation preferentially occurs from the high-vibrational quantum states. These effects have been observed in the master equation modeling of vibrational relaxation of N_2 at $T = 8000$ K.[1]

Recent experimental measurements of vibrational relaxation rates in oxygen at $T = 300$ K (Refs. 3–5) seemingly confirm that this effect does exist (see Fig. 2), at least at the low translational temperatures. However, extrapolation of this conclusion to high temperatures, based on the results of calculations,[1] has no firm theoretical basis. First, in their calculations of vibration–translation (V–T) and vibration–vibration (V–V) rates, the authors of Ref. 1 applied first-order perturbation theory (SSH theory[6]) to the high-energy molecular collisions, and also to multiquantum processes. However, it is well known that first-order perturbation theory is not applicable to calculations of large transition probabilities, which can become

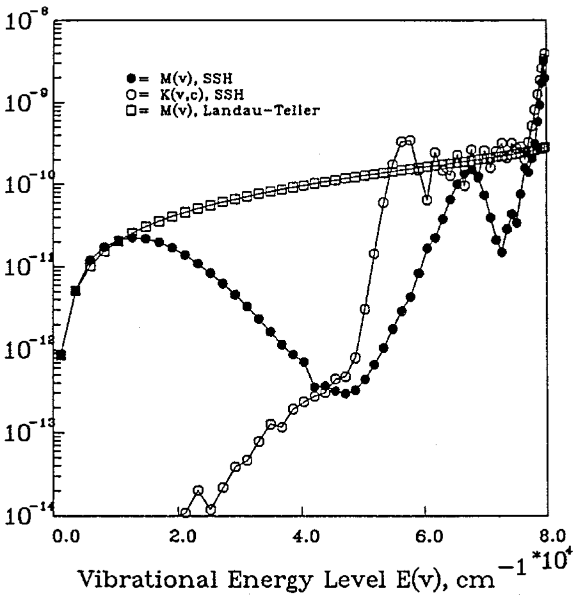

Fig. 1 Transition moment of Eq. (1) $M(v)$, based on the transition rates,[1] for nitrogen at $T = 4000$ K. Open circles show the rate of dissociation.[2]

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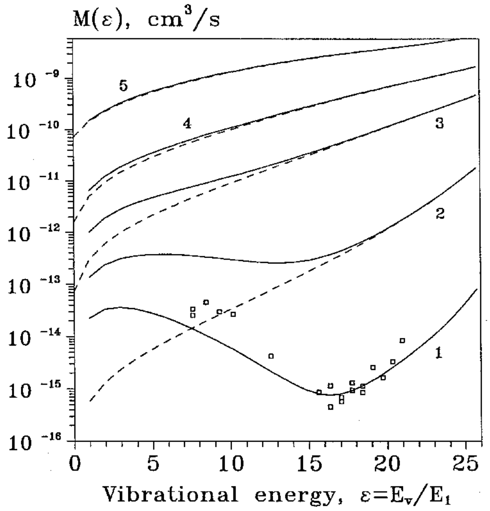

Fig. 2 Transition moment of Eq. (3) $M(\varepsilon)$ based on the FHO relaxation rates for O_2 (Ref. 7) at $T_v = 300$ K. Solid line, both $V-T$ and $V-V$ processes are considered; dashed line, $V-T$ processes only; symbols and experimental data at T = 300 K.[3–5] 1, T = 300 K; 2, T = 1000 K; 3, T = 3000 K; 4, T = 5000 K; and 5, T = 10,000 K.

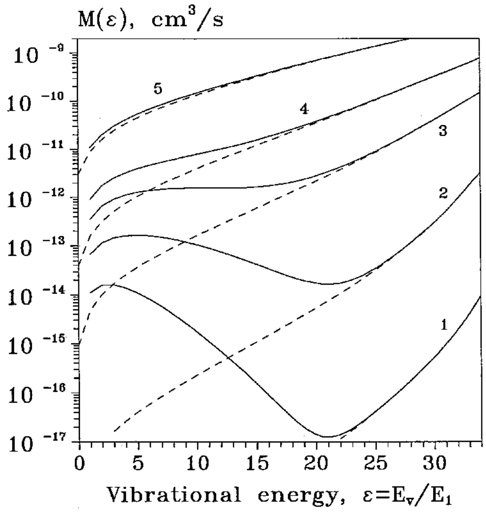

Fig. 3 Transition moment of Eq. (3) $M(\varepsilon)$ based on the FHO relaxation rates for N_2 (Ref. 7) at $T_v = 300$ K. Solid line, both $V-T$ and $V-V$ processes are considered; dashed line, $V-T$ processes only. 1, T = 300 K; 2, T = 1000 K; 3, T = 3000 K; 4, T = 5000 K; and 5, T = 10,000 K.

comparable to unity at high collision energies. Also, it has been recently shown that multiquantum vibrational energy transfer occurs not by a first-order mechanism,[7] and one has to use an N-term wave function expansion to evaluate the probability of a process that transmits N vibrational quanta.[8] Finally, the intermolecular potential used in Ref. 1 is quite different from the potential obtained from ab initio calculations.

In the present paper, we analyze the behavior of the vibrational energy diffusion coefficient and the conditions for the existence of the bottleneck effect over a large range of translational and vibrational temperatures. The state-specific vibrational energy transfer rate coefficients are calculated on the basis of nonperturbative forced harmonic oscillator analytic theory (FHO)[7,9–13] that gives an exact analytic solution of the Schrodinger equation instead of expanding the wave functions in a series. The intermolecular potentials used in the calculations fit ab initio potentials used in three-dimensional close-coupled semiclassical calculations.[14–16] The $V-T$ and $V-V$ rates predicted by the FHO theory are in very good agreement both with the results of these three-dimensional calculations for N_2–N_2, O_2–O_2, and N_2–O_2 and with available experimental data in oxygen[3–5] (e.g., see Refs. 7 and 12).

II. Results and Discussion

Figures 2 and 3 show the transition moment $M(\varepsilon)$, similar to $M(v)$ given by Eq. (1)

$$M(\varepsilon_v) = \frac{1}{2}\sum_w \frac{(E_v - E_w)^2}{E_1^2}\cdot K(v, w) = \frac{1}{2}\sum_w (\varepsilon_v - \varepsilon_w)^2\cdot K(v, w) \tag{3}$$

calculated for N_2 and O_2 at different translational temperatures. In Eq. (3) and in Figs. 2 and 3, $E_v = \omega_e v[1 - x_e(v + 1)]$ is the energy of vibrational level v in Kelvin, and $\varepsilon_v = E_v/E_1$ is the dimensionless vibrational energy. One can see that, indeed, $V-V$ exchange results in a dramatic increase in $M(\varepsilon)$ at low temperatures, in agreement with experimental data (see Fig. 2). However, at high translational temperatures such as $T/E_1 \gtrsim 1.5$ ($T \gtrsim 3000$ K for O_2 and $T \gtrsim 5000$ K for N_2) the effect becomes much smaller (compare with Fig. 1). One can see that the high-temperature $V-V$ rates calculated for realistic intermolecular potentials are much smaller than obtained in Ref. 1.

Note that in the presence of $V-V$ exchange the transition moment, given by Eqs. (1) and (3) cannot be interpreted simply as a diffusion coefficient in the vibrational energy space, as in the case when $V-T$ relaxation dominates. In the high-temperature limit, when $T/E_1 >> 1$, the master equation for the populations of vibrational levels of diatomic molecules

$$\begin{aligned}\frac{1}{N}\frac{\mathrm{d}f_v}{\mathrm{d}t} &= \sum_{v',w,w'} k(w, w' \to v, v')f_w f_{w'} \\ &\quad - \sum_{v',w,w'} k(v, v' \to w, w')f_v f_{v'}\end{aligned} \tag{4}$$

reduces to an integro-differential equation[17,18]

$$\begin{aligned}\frac{1}{N}\frac{\partial f(\varepsilon, t)}{\partial t} &= \frac{\partial}{\partial \varepsilon} \\ &\times \left\{\begin{aligned}&\left[\frac{\partial f(\varepsilon)}{\partial \varepsilon} - f(\varepsilon)\frac{\partial\, \ell n\, f_{\mathrm{eq}}(\varepsilon)}{\partial \varepsilon}\right]\int \mathrm{d}\varepsilon'\cdot f(\varepsilon')M_1(\varepsilon, \varepsilon') \\ &-f(\varepsilon)\int \mathrm{d}\varepsilon'\cdot M_2(\varepsilon, \varepsilon')\left[\frac{\partial f(\varepsilon')}{\partial \varepsilon'} - f(\varepsilon')\frac{\partial\, \ell n\, f_{\mathrm{eq}}(\varepsilon')}{\partial \varepsilon'}\right]\end{aligned}\right\}\end{aligned} \tag{5}$$

where

$$M_1(\varepsilon, \varepsilon') = \frac{1}{2}\sum_{w,w'} k(v, v' \to w, w')\cdot(\varepsilon_v - \varepsilon_w)^2 \tag{6}$$

$$M_2(\varepsilon, \varepsilon') = \frac{1}{2}\sum_{w,w'} k(v, v' \to w, w')\cdot|\varepsilon_v - \varepsilon_w|\cdot|\varepsilon_{v'} - \varepsilon_{w'}| \tag{7}$$

Equation (5) may be further reduced to a diffusion-type equation if one assumes that the $V-V-T$ rate matrix $k(v, v' \to w, w')$ can be presented as two separate matrices: 1) $V-T$ mode rates $k_{VT}(v \to w)$ and 2) $V-V$ mode rates $k_{VV}(v, v' \to v + \Delta v, v' - \Delta v)$:

$$\begin{aligned}\frac{1}{N}\frac{\partial f(\varepsilon, t)}{\partial t} &\cong \frac{\partial}{\partial \varepsilon}\left\{[D_{VT}(\varepsilon) - D_{VV}(\varepsilon, t)]\right. \\ &\quad \left.\times\left[\frac{\partial f(\varepsilon)}{\partial \varepsilon} - f(\varepsilon)\frac{\partial\, \ell n\, f_{\mathrm{eq}}(\varepsilon)}{\partial \varepsilon}\right]\right\}\end{aligned} \tag{8}$$

where

$$D_{VT}(\varepsilon) \cong \frac{1}{2}\sum_{\Delta v} k_{VT}(v \to v + \Delta v)\cdot(\varepsilon_v - \varepsilon_{v+\Delta v})^2 = Z\,\frac{\langle(\Delta\varepsilon)^2\rangle}{2} \tag{9}$$

$$\begin{aligned} D_{VV}(\varepsilon, t) &\cong \frac{1}{2}\sum_{\Delta v, v'} f_{v'}\cdot k_{VV}(v, v' \to v + \Delta v, v' - \Delta v) \\ &\times |\varepsilon_v - \varepsilon_{v+\Delta v}|\cdot(|\varepsilon_{v'} - \varepsilon_{v'-\Delta v}| - |\varepsilon_v - \varepsilon_{v+\Delta v}|) \\ &= Z\,\frac{\langle|\Delta\varepsilon|\cdot(|\Delta\varepsilon'| - |\Delta\varepsilon|)\rangle}{2} \end{aligned} \tag{10}$$

In Eqs. (9) and (10), Z is the gas-kinetic collision frequency. In the absence of the V-V exchange, $D_{VV} = 0$ and Eq. (8) becomes the well-known Fokker-Planck diffusion equation.[19] Both Eqs. (5) and (8) are valid only if

$$(E_1/T)^2\langle(\Delta\varepsilon)^2\rangle << 1 \tag{11}$$

and also if $T/E_1 >> 1$, $\langle\Delta\varepsilon\rangle/\varepsilon << 1$.

From Eqs. (9) and (10), one can see that 1) the overall diffusion coefficient $D = D_{VT} - D_{VV}$ may change sign, depending on the vibrational distribution function $f(\varepsilon)$ (i.e., on time) and on vibrational energy ε and 2) $|D(\varepsilon, t)| = |D_{VV}(\varepsilon) - D_{VT}(\varepsilon, t)| < M(\varepsilon)$. Therefore, the effect of V-V exchange on the diffusion flux is even less than one might assume from Figs. 2 and 3. Figures 4 and 5 demonstrate that if $T/E_1 \geq 1.5$-2.0, the contribution of the V-V processes to the overall diffusion coefficient D does not exceed 10% and dramatically decreases with temperature. In other words, at the high temperatures vibration-vibration exchange between the molecules of the same species can be neglected.

The effect of the V-V exchange at low temperatures, when $T/E_1 < 1$, is certainly much more pronounced, especially at high vibrational temperatures (see Figs. 4 and 5). Although the diffusion Eq. (8) is not applicable at these conditions, it can nevertheless qualitatively predict the time evolution of the distribution function. For example, the behavior of the overall diffusion coefficient $D = D_{VT} - D_{VV}$ at $T = 1000$ K, $T_v = 5000$ K, shown in Fig. 5, predicts depopulation of the low and the high vibrational levels of O_2, and overpopulation of the middle levels, where $D < 0$, during the relaxation process at $T_v > T$. This is a well-known result of vibrational kinetics of anharmonic oscillators. The diffusion theory of vibrational relaxation at the low translational temperatures, when $T/E_1 << 1$, is based on a different form of the Fokker-Planck equation, and was developed in the 1970s (e.g., see Refs. 20 and 21 and references therein). It also shows remarkably good agreement with the exact master equation calculations.

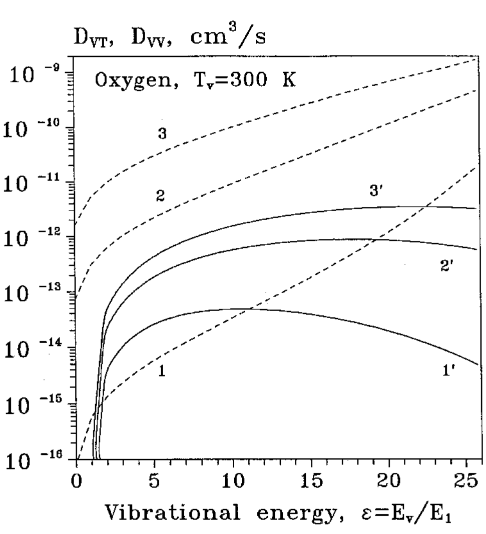

Fig. 4 Vibrational energy diffusion coefficients because of V-T (dashed lines) and V-V (solid lines) processes. Oxygen at T_v = 300 K. 1,1', T = 1000 K; 2,2', T = 3000 K; and 3,3', T = 5000 K.

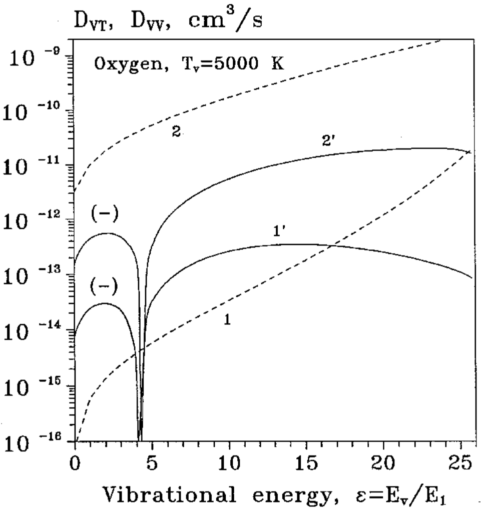

Fig. 5 Vibrational energy diffusion coefficients because of V-T (dashed lines) and V-V (solid lines) processes. Oxygen at T_v = 5000 K. 1,1', T = 1000 K and 2,2', T = 5000 K. Symbol (-) shows the region where D_{VV} becomes negative.

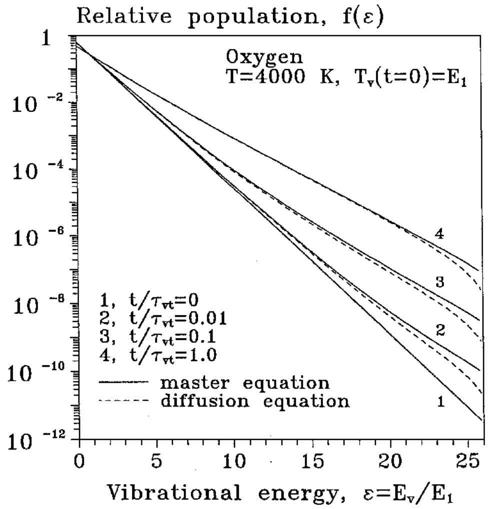

Fig. 6 Vibrational distribution function of oxygen during the relaxation at constant temperature T = 4000 K.

To verify the applicability of the diffusion approximation (8) at very high temperatures, when $T/E_1 >> 1$, we considered the problem of vibrational relaxation behind a shock wave using two different approaches: 1) exact master Eq. (4) and 2) diffusion Eq. (8) with the diffusion coefficient given by Eqs. (9) and (10). In both cases, the same V-T and V-V rates have been used. To account for the molecular dissociation that is assumed to occur from the high vibrational levels, the equivalent constraints of total absorption have been imposed:

$$f(v = v_{\text{diss}}) = 0 \quad \text{and} \quad f(\varepsilon = \varepsilon_{\text{diss}}) = 0 \tag{12}$$

A Boltzmann distribution with vibrational temperature $T_v = E_1$ was assumed at $t = 0$.

The results of the calculations for oxygen at the constant translational temperatures T = 4000 and 8000 K are shown in Figs. 6 and 7. One can see that at T = 4000 K the diffusion approximation is applicable, except for the high vibrational levels near the dissociation limit. At T = 8000 K the two ap-

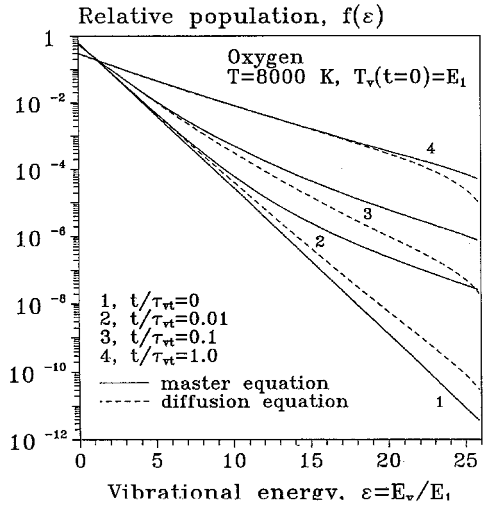

Fig. 7 Vibrational distribution function of oxygen during the relaxation at constant temperature T = 8000 K.

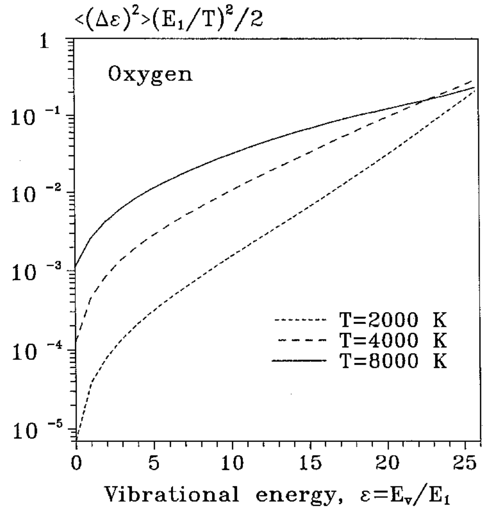

Fig. 8 Normalized vibrational energy diffusion coefficient D_{VT} in oxygen.

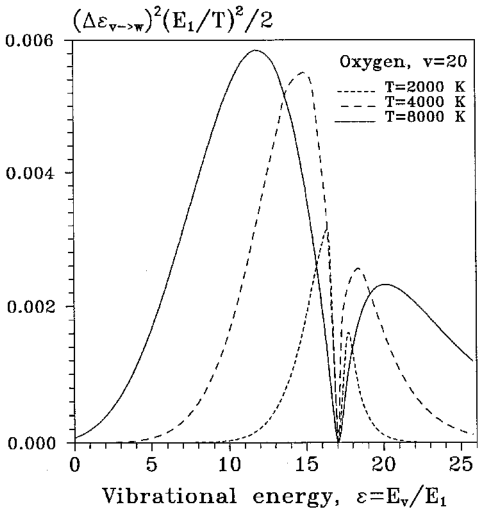

Fig. 9 Distribution of the V–T relaxation products of $O_2(v = 20)$ at different translational temperatures.

proaches give different results, even at much lower energies, especially for $t/\tau_{VT} << 1$ (τ_{VT} is the Landau–Teller vibrational relaxation time). In both cases, the high vibrational level populations given by the master equation quickly get to equilibrium with translational temperature T, so that the boundary condition (12) has almost no effect on the distribution function. The criterion of Eq. (11) that limits the applicability of the diffusion approximation, is satisfied in both cases, excluding high vibrational energies $\varepsilon \cong \varepsilon_{diss}$ (see Fig. 8). However, Fig. 9 demonstrates that the reason for the difference between the two model predictions at the high temperature is multiquantum relaxation. One can see that the products of the V–T relaxation of oxygen initially at the vibrational level $v = 20$ spread much wider over the vibrational energy axis as the temperature increases, so that $\langle\Delta\varepsilon\rangle/\varepsilon \sim 1$. This makes the high-temperature ($T/E_1 >> 1$) relaxation in air an essentially nonlocal process, the diffusion approximation therefore being inapplicable over the broad range of vibrational energies. We note, however, that the difference between the two approaches (master equation vs diffusion approximation) almost ceases to exist at $t/\tau_{VT} \geq 1$, the distribution function becoming Boltzmann-like, except for the high energies within $\Delta\varepsilon \sim T/E_1$ from the dissociation limit.

Figure 7 looks very similar to the results of master equation modeling of the high-temperature relaxation using the FHO model and the first-order rate model (SSH theory, single-quantum processes only).[13,22] The latter also strongly underestimates the populations of the high vibrational levels during the relaxation at $t/\tau_{VT} \leq 1$, despite predicting much greater V–T rates than given by the FHO model. We conclude that the failure of the first-order models to adequately describe the distribution function at conditions of extreme vibrational disequilibrium is mainly because of their neglect of multiquantum relaxation, not just because they predict the single-quantum rates incorrectly. Finally, Figs. 6 and 7 show that the use of diffusion approximation for modeling of relaxation and dissociation at the high vibrational levels such as $\varepsilon_v \geq \varepsilon_{diss} - T/E_1$, is not justified, as also pointed out in Ref. 2.

As expected, in the present calculations only, a small difference has been found between the distribution function $f_v(t)$ formed by the V–T relaxation only, and the one controlled by both V–T and V–V exchange. No bottleneck effect that would create a bimodal vibrational distribution[1,2] has been observed.

These results can be also applied to interpretation of the thermal dissociation data ($T_v = T$) at temperatures that are not very high $T/E_1 \sim 1$–3, when dissociation preferentially occurs from the high vibrational levels.[22] At these conditions, the dissociation is controlled by the rate of activation of the high vibrational levels such as $\varepsilon_v \cong \varepsilon_{diss}$. It is well known that the rate of the thermal molecular dissociation is greater when the collision partner is another molecule, rather than an atom. For example, the ratio $k_{diss}(O_2–O_2)/k_{diss}(O_2–Ar)$ changes from 30–40 at T = 3500 K to 5–10 at T = 7000 K.[19] The fact that V–V exchange has almost no contribution in the molecular activation at the high temperatures shows that it cannot be responsible for the dissociation rate increase in diatom–diatom collisions. Also, calculations of the activation rate

$$k_{act}(T) = \sum_{v} k_{VT}(v \rightarrow v_{diss})\cdot f_v(T) \qquad (13)$$

for O_2–O_2 and O_2–Ar collisions give rather close results (within a factor of 2–3 in this temperature region), which shows that the slightly different collision-reduced masses and intermolecular potentials also do not explain the observed effect. The activation rate of Eq. (13) can be interpreted as the rate of dissociation for the total absorption condition (12). This suggests that the rotational energy of the collision partner, disregarded in the FHO vibrational energy transfer model, must play an important role in the molecular activation at the high vibrational levels. A qualitative estimate of the role of rotations predicts about an order of magnitude increase in the diatom–diatom dissociation rate.[19] More theoretical effort is needed to obtain a better insight into this problem.

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