Three-dimensional nonperturbative analytic model of vibrational energy transfer in atom–molecule collisions

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A three-dimensional semiclassical analytic model of vibrational energy transfer in collisions between a rotating diatomic molecule and an atom has been developed. The model is based on analysis of classical trajectories of a free-rotating (FR) molecule acted upon by a superposition of repulsive exponential atom-to-atom potentials. The energy transfer probabilities have been evaluated using the nonperturbative forced harmonic oscillator (FHO) model. The model predicts the probabilities for vibrational energy transfer as functions of the total collision energy, orientation of a molecule during a collision, its rotational energy, and impact parameter. The model predictions have been compared with the results of three-dimensional close-coupled semiclassical trajectory calculations using the same potential-energy surface. The comparison demonstrates not only remarkably good agreement between the analytic and numerical probabilities across a wide range of collision energies, but also shows that the analytic FHO-FR model correctly reproduces the probability dependence on other collision parameters such as rotation angle, angular momentum angle, rotational energy, impact parameter, and collision reduced mass. The model equally well predicts the cross sections of single-quantum and multiquantum transitions and is applicable up to very high-collision energies and quantum numbers. Most importantly, the resultant analytic expressions for the probabilities do not contain any arbitrary adjustable parameters commonly referred to as “steric factors.” The model provides new insight into kinetics of vibrational energy transfer and yields accurate expressions for energy-transfer rates that can be used in kinetic modeling calculations. © 1998 American Institute of Physics. [S0021-9606(98)01642-0]

I. INTRODUCTION

Vibrational energy-transfer processes in collisions of diatomic molecules play an extremely important role in gas discharges, molecular lasers, plasma chemical reactors, high-enthalpy gas dynamic flows, and in the physics of the upper atmosphere. In these nonequilibrium environments, the energy loading per molecule may be as high as 0.1–5.0 eV, while disequipartition among translational, vibrational, and electronic energy modes of heavy species, and with the free electron energy, may be very strong. This often results in development and maintaining of strongly nonequilibrium molecular vibrational energy distributions, which induce a variety of energy-transfer processes among different energy modes and species, chemical reactions, and ionization.1–4

The rates of these processes are determined by the populations of high-vibrational levels of molecules, which are often controlled by vibration–translation (V–T) processes

\[ AB(\nu) + M \rightarrow AB(\nu^\prime) + M, \]  

(1)

and vibration–vibration (V–V–T) processes

\[ AB(\nu_1) + CD(\nu_2) \rightarrow AB(\nu_1^\prime) + CD(\nu_2^\prime). \]  

(2)

In Eqs. (1) and (2), \( AB, CD, \) and \( M \) represent diatomic molecules and an atom, respectively, and \( \nu_1, \nu_2, \nu_1^\prime, \) and \( \nu_2^\prime \) are vibrational quantum numbers.

Quantitative data on the mechanisms and kinetic rates of these processes are needed for numerous practical applications, including novel chemical technologies, environmental pollution control, and radiation prediction in aerospace propulsion flows, in high-altitude rocket plumes and behind shock waves. There exists an extensive literature on the experimental study of V–T and V–V–T energy transfer, including recent state-specific rate measurements for highly vibrationally excited molecules, such as NO, O2, and CO.5–9

However, for many high-temperature and high vibrational quantum number energy-transfer processes, the experimental rate data are still unavailable. As a result, most such rates used in applied kinetic modeling are based on theoretical scattering calculations. Among numerous theoretical rate models available, one can separate the following major approaches: (i) Fully quantum calculations, (ii) classical, quasiclassical, and semiclassical numerical trajectory calculations, and (iii) analytic methods.

Since the exact quantum calculations are rather computationally laborious, they have been usually made for a simplified model of collinear collisions of harmonic oscillators and used as tests for more approximate approaches.10–12

However, some three-dimensional calculations of the state-specific vibrational energy-transfer rates for \( \mathrm{O}_2–\mathrm{O}_2 \) using vibrational close-coupling infinite-order sudden approximation (VCC-IOSA) have been recently published.13

Classical and quasiclassical trajectory methods, such as the methods used for calculations of vibrational relaxation rates for \( \mathrm{O}_2–\mathrm{Ar}, \)14 \( \mathrm{N}_2–\mathrm{N}, \) and \( \mathrm{O}_2–\mathrm{O}, \)15,16 are applicable only for calculation of rather large transition probabilities. For accurate predictions of small transition probabilities \( P \ll 1, \) a
large number of collision trajectories, $N \sim 1/P$, have to be averaged.

Among semiclassical calculations, one can mention the close-coupled method developed by Billing and validated by comparison with the exact quantum calculations, as well as with experimental data. Trajectory calculations by this method have been made for a number of species such as H$_2$, N$_2$, O$_2$, and CO$^{18–23}$ in a wide range of collision energies and vibrational quantum numbers. These results comprise perhaps the most extensive and consistent vibrational energy-transfer rate database.

In addition to some fundamental problems encountered in calculations by these advanced methods (such as the choice of the three-dimensional potential-energy surface), their results are often difficult to interpret and use in kinetic modeling calculations. First, it is not always possible to identify the key energy transfer mechanisms that control the cross sections obtained. Second, the number of state-specific rates used as entries in modern master equation kinetic models for studies of strongly nonequilibrium gases and plasmas may reach $10^4–10^5$. Even if some of these rate data are available from three-dimensional computer calculations, one has to rely on curve fitting, unreliable extrapolation, or inaccurate analytic parametrization to incorporate the rates into the model. As a result, such kinetic models do not provide new insight into kinetics, have limited applicability, and lack predictive capability.

Approximate analytic rate expressions are also widely used in kinetic modeling, mostly because of their simplicity. However, available analytic models have serious inherent flaws that make them much less reliable and accurate compared to numerical scattering calculations. First, most of these models, such as the Schwartz, Slawsky, Herzfeld (SSH) theory, Rapp–Englander–Golden model, Sharma–Brau theory etc.24–27 are based on first-order perturbation theory (FOPT), and therefore, cannot be applied at high-collision energies, high-quantum numbers, and for multi-quantum processes $|i−f|>1$ in Eqs. (1) and (2). An exception is the nonperturbative forced harmonic oscillator (FHO) model,28–31 which takes into account the coupling of many vibrational states during a collision and is, therefore, applicable for such conditions. Second, analytic models are typically developed only for collinear collisions of nonrotating molecules. A procedure commonly used to account for the effects of realistic three-dimensional collisions and molecular rotation is the introduction of adjustable correction parameters (steric factors) into the resultant rate expression.32 These coefficients, which are assumed to be temperature independent, have very little or no theoretical basis and are found from comparison of a simple model with experiments or three-dimensional calculations.

There have been various attempts to develop nonempirical expressions for the steric factors and also to incorporate the effect of rotation into analytic models.32–35 In most of them, the simplifying assumptions made, such as analyzing of collisions of arbitrarily oriented, but nonrotating, molecules,32 or, on the contrary, considering only collisions of rapidly rotating "breathing spheres" (i.e., isotropic three-dimensional oscillators),33–35 were unrealistic. In addition, the coupled effects of orientation of colliding partners, molecular rotation, and nonzero impact parameter collisions have been analyzed separately. Finally, the procedure of comparison between the experimental relaxation rates and the analytic rates corrected for noncollinear orientation and rotation, used by some authors to validate theoretically obtained values of the steric factors, is hardly conclusive. It such cases, the agreement obtained might well be due to the formal adjustment of the intermolecular potential parameters used, i.e., to a curve fitting. The only credible procedure for analytic model validation would be comparing its predictions with the results of three-dimensional numerical calculations made for the same potential-energy surface.

The present paper addresses development of a semiclassical analytic vibrational relaxation model that incorporates the effects of three-dimensional collisions and molecular rotation. As a first step, we analyze energy transfer in collisions between a diatomic molecule and an atom. The two main goals of this study are (i) analytic transition probabilities that must be in agreement with trajectory calculations and (ii) expressions for transition probabilities that can be easily incorporated in nonequilibrium kinetic models. Such a model gives new insight into mechanisms of vibrational relaxation, as well as bridging the gap between state-of-the-art theoretical scattering techniques and their use for practical applications.

II. COLLISION TRAJECTORIES AND TRANSITION PROBABILITIES

The method used in the present paper is somewhat similar to the approach developed by Skrebkov and Smirnov,36 which is perhaps the most advanced of available analytic models. They calculated the trajectory of a rotating diatomic molecule colliding with an atom when all three atoms are moving in the same plane, and used classical mechanics perturbation theory to evaluate the average vibrational energy transmitted in a collision. They also assumed a local exponential dependence of the intermolecular potential on all collision coordinates $q_j, U(q_j) \sim \exp[-\alpha(q_j - q_{0j})]$, in the vicinity of the turning point. This constraint forces both the translational motion and the rotation to stop at the turning point, which makes the motion equations tractable but does not allow incorporation of molecular rotation in three dimensions. In the present paper, we uncouple the translational motion and the three-dimensional rotation, assuming the latter to be unaffected by the collision, i.e., free. Then the only effect of rotation on the collision trajectory is the periodic modulation of the interaction potential. Note that the assumption of free rotation is quite similar to the basic assumption made in all semiclassical theories, which evaluate the translational–rotational trajectory uncoupled from the vibrational motion of the oscillator. Also, instead of relying on perturbation theory, we will use the exact semiclassical solution of the Schrödinger equation (the FHO theory$^{28–31}$) to evaluate the vibrational transition probabilities. This will expand the applicability of the model to high-collision energies and allow prediction of multiquantum vibrational transition rates.
Let us analyze the dynamics of collisions between a rotating symmetric diatomic molecule and an atom. First consider a head-on (zero impact parameter) collision (Fig. 1). For the pairwise atom-to-atom interaction described by a repulsive exponential function, \( U(R) = A \exp(-\alpha R) \), where \( R_i \) is the distance between the atoms, the atom–molecule interaction potential can be written as follows:

\[
U(R, r, \vartheta, \varphi) = 2A e^{-\alpha R} \cosh \left[ \frac{\alpha r}{2} \cos \vartheta \cos \varphi \right].
\]  

(3)

In Eq. (3), \( R \) is the center-of-mass distance, \( r \) is the separation of atoms in a molecule, \( \vartheta \) is the rotation angle, and \( \varphi \) is the angle between the plane of rotation and the radius vector \( \mathbf{R} \) (see Fig. 2). To derive Eq. (3), we used the approximation \( (R^2 + r^2/4 + R r \cos \vartheta)^{1/2} \approx R + r \cos \vartheta/2 \). Let us assume that the rotation is free, that is, neither the magnitude nor the direction of the angular momentum vector change in a collision. That gives \( \vartheta(0) = \vartheta_0 + \Omega t \), \( \varphi(0) = \varphi_0 \), where \( \Omega \) is the constant angular velocity of molecular rotation, and the subscript ‘0’ means ‘at the point of maximum interaction,’ where \( U \) is maximum. To calculate the semiclassical trajectory \( R(t) \), we assume \( r(t) = r_e \), where \( r_e \) is the equilibrium atom separation, so that

\[
U(R, r_e, \vartheta, \varphi) = 2A e^{-\alpha R(t)} \cosh \left[ \frac{\alpha r_e}{2} \cos \vartheta \cos \varphi \right] = B e^{-\alpha R(t)} \frac{\cosh[d \cos(\vartheta_0 + \Omega t) \cos \varphi_0]}{\cosh[d \cos \vartheta_0 \cos \varphi_0]},
\]  

(4)

where \( d = \alpha r_e/2 \geq 1 \). \( \tilde{R}(t) = R(t) - R_0 \), and \( B = 2A \times \exp(-\alpha R_0) \cosh[d \cos \vartheta_0 \cos \varphi_0] \). One can see that the potential (4) consists of the exponential translational part modulated by the periodic rotational factor. If the rotation is not very rapid, the modulation can substantially change the shape of the time-dependent perturbation, \( U(\tilde{R}, t) \). The classical equation of motion for this potential, \( \dot{m}\tilde{R}(t) = - \partial U(\tilde{R}, t)/\partial \tilde{R} \), can be easily solved if the rotation is slow, so that the potential \( U(\tilde{R}, r_e, t) = U(\tilde{R}, t) \) can be expanded near the point of maximum interaction, \( R_0 \)

\[
m\tilde{R}(t) = m \dot{R}(t) = aB e^{-\alpha R(t)} \left[ 1 - \tanh(d \cos \vartheta_0 \cos \varphi_0) \right] \times d \sin \vartheta_0 \cos \vartheta_0 = \Omega t \]

\[
= aB e^{-\alpha R(t)} \left[ 1 - g(\vartheta_0, \varphi_0) \right] d\Omega t,
\]  

(5)

where \( g(\vartheta_0, \varphi_0) = \tanh(d \cos \vartheta_0 \cos \varphi_0)d \sin \vartheta_0 \cos \vartheta_0 = v/2 \sin 2\vartheta_0 \cos \vartheta_0 \), and \( m \) is the collision reduced mass. Solving Eq. (5), one obtains

\[
e^{-\alpha R(t)} = \frac{1 + g(\vartheta_0, \varphi_0) d\Omega t}{\cosh^2 \left[ at/2m \right]} \cosh \left[ d \cos(\vartheta_0 + \Omega t) \cos \varphi_0 \right]
\]

(6)

and

\[
U(t) = \frac{B}{\cosh^2 \left[ at/2m \right]}; \quad B = U(0).
\]  

(7)

Note that the trajectory of Eq. (7) is identical to the well-known result of one-dimensional theory if one takes parameter \( B \) (the maximum interaction energy) equal to the translational kinetic energy at infinity, \( B = E_w = mv^2/2 \). In our case, however, \( B \) depends on the molecular orientation and its rotational energy and is not necessarily equal to \( E_{tr} \). Indeed, the full derivative of the interaction energy given by Eq. (4) is

\[
\frac{D}{D t} \left( \frac{DU(\tilde{R}, t)}{D t} \right) = \frac{\partial U}{\partial R} \tilde{R} + \frac{\partial U}{\partial t} \dot{t} + \frac{\partial U}{\partial \vartheta} \vartheta + \frac{\partial U}{\partial \varphi} \varphi \quad B = \int_0^t \frac{DU}{D t} \, dt.
\]  

(8)

In Eq. (8), the first term in the right-hand-side is the work of the potential force and the second is the interaction energy change due to the free rotation, which depends only on time. Using Eqs. (4), (6), and (8), one can obtain an implicit expression for \( B \)

\[
B = E - E_{rot} - \frac{\xi}{2} g(\vartheta_0, \varphi_0)^2 E_{rot}
\]

\[
+ \sqrt{\xi} \cdot g(\vartheta_0, \varphi_0) \sqrt{2E_{rot}B},
\]  

(9)

where \( E = E_w + E_{rot} \) is the total energy of a molecule at infinity, \( E_{rot} = m_0 \Omega^2 r_e^2/2 \) is its rotational energy, \( m_0 \) is the oscillator reduced mass, and \( 2\xi = m/m_0 \) is the ratio of the collision and oscillator reduced masses.

For nonzero impact parameter collisions, the trajectory can be found by taking into account only radial relative motion of the colliding partners, \( R(t) \), in the vicinity of the maximum interaction point, as shown in Fig. 2. Then the problem is reduced to the case considered above by replacing the kinetic energy \( E - E_{rot} \) by the energy of the radial motion, \( E_{rad} = (E - E_{rot}) \left[ 1 - b^2/R_0(t)^2 \right] \equiv (E - E_{rot})(1 - b^2/R_0^2) \) (the...
and orientation of collision partners, characterized by a three-dimensional trajectory with the same total collision energy. Therefore, Eq. (7) for the trajectory remains unchanged while parameter $B$ becomes

$$B = (E - E_{\text{rot}}) \left(1 - \frac{b^2}{R_0^2}\right) - \frac{\xi}{2} g(\vartheta_0, \varphi_0)^2 E_{\text{rot}}$$

$$+ \sqrt{\xi} \cdot g(\vartheta_0, \varphi_0) \sqrt{2E_{\text{rot}} B}.$$  \hspace{1cm} (9a)

Introducing dimensionless parameters $\beta = B/E$, $\epsilon = E_{\text{rot}}/E$, and $y = b^2/R_0^2$, and solving Eq. (9a) for $\gamma = \sqrt{\beta}$, one has

$$U(t) = \frac{E \gamma^2}{\cosh^2 \left[\gamma \alpha \sqrt{\frac{E}{2m}}\right]}.$$  \hspace{1cm} (9b)

$$\gamma(\epsilon, y, \vartheta_0, \varphi_0) = \sqrt{\beta}$$

$$\approx \max \left[0, -\frac{\sin 2\vartheta_0 \cos \varphi_0}{2} \sqrt{\xi} \epsilon \right]$$

$$+ \sqrt{(1 - \epsilon)(1 - y)}.$$  \hspace{1cm} (10)

Equation (9b) describes a parametric set of three-dimensional trajectories with the same total collision energy $E$ and various values of rotational energy, impact parameter, and orientation of collision partners, characterized by a single factor $\gamma = (\epsilon, y, \vartheta_0, \varphi_0)$, which is given by Eq. (10). The factor $E \gamma^2$ in Eq. (9b) can be interpreted as the effective collision energy. One can see that at $\epsilon = y = \vartheta_0 = \varphi_0 = 0$, one has $\gamma = 1, E = E_{\text{rot}}$, and the trajectory coincides with the one-dimensional result for a head-on collinear collision of a nonrotating molecule with an atom.37

The applicability of Eqs. (9b) and (10) is limited to relatively slow molecular rotation by an approximation made in Eqs. (3) and (4), $g(\vartheta_0, \varphi_0) d\Omega \tau = 1$, where $\tau = 2\alpha v_\infty$ is the time scale for the interaction energy change. Therefore, the described approach is valid only if

$$\epsilon = E_{\text{rot}}/E \ll \frac{1}{2} \left(1 - \gamma^2/2\right).$$  \hspace{1cm} (11)

so that the collision trajectory of a rapidly rotating molecule cannot be accurately predicted, especially at large impact parameters. However, the contribution of such collisions to the overall transition probability as a function of the total collision energy $E$ is expected to be small. Indeed, for such collisions (i) the available translational energy of radial motion is small, $E_{\text{tr}} = E(1 - b^2/R_0^2) - E_{\text{rot}} \ll E$, and (ii) the potential-energy surface of Eq. (4) becomes nearly isotropic due to the rapid rotation so that the breathing sphere model 34 become applicable. As is well known,39 the vibrational transition probabilities in slow repulsive collisions of breathing spheres (i.e., isotropic three-dimensional oscillators) drop exponentially as the collision energy $E_{\text{tr}}$ decreases. Therefore, in the present paper we disregard such collisions. Later we will show that this assumption is consistent with the results of the three-dimensional trajectory calculations.

Having calculated the free rotation collision trajectory (9b) and (10), now we can evaluate the semiclassical energy transfer probabilities $P_{ij}$, where $i$ and $f$ are initial and final vibrational quantum numbers, respectively. For this we will use the FHO theory,28–31 a nonperturbative analytic model, originally developed for collinear collisions of a nonrotating diatomic molecule and an atom. This model is based on the exact solution of the Schrödinger equation for the intermolecular potential $U(R, r, \vartheta, \varphi)$ linearized in $r$ and, therefore, takes into account the coupling of all vibrational quantum states during a collision. It is applicable up to high-collision energies and vibrational quantum numbers, as well as for multiquantum transitions. The scaling law predicted by this model, i.e., the probability dependence on the vibrational quantum numbers, is independent of the potential and is given by the following relation:

$$P_{ij} = \left(J_s^2(2\sqrt{n_s} Q)\right)^{\frac{(n_i)^2}{(s!)^2}} Q^s$$

$$\times \exp \left[ -\frac{2n_s}{s+1} Q - \frac{n_s^2}{(s+1)^2(s+2)} Q^2 \right],$$

$$s = |i - f|, \quad n_s = \left[\max(i,f)!/\min(i,f)!\right]^{1/4}.$$  \hspace{1cm} (12)

In Eq. (12), $J_s$ is the Bessel function of the $s$th order, and the potential-dependent parameter $Q = AE/h \omega$ is the average dimensionless energy (i.e., the average number of quanta) transferred to the initially nonvibrating classical oscillator in a collision28,29

$$Q = \left|\frac{\langle 1|\tilde{r}|0\rangle^2}{\hbar^2}\right| \int_{-\infty}^{\infty} \frac{\partial U(\tilde{r}, \tilde{r}, t)}{\partial \tilde{r}} e^{int} dt \bigg|.$$  \hspace{1cm} (13)

In Eq. (13), $\tilde{r} = r - r_e$, and $\langle 1|\tilde{r}|0\rangle^2 = \hbar/2m_0 \omega$ is the squared matrix element of the transition $0 \rightarrow 1$. Using Eqs. (4) and (9b), one obtains

FIG. 2. Schematic of a nonzero impact parameter atom–molecule collision.
where

\[
Q(E,\varepsilon,\gamma,\vartheta_0,\varphi_0) = \langle \hat{\gamma} | \hat{\gamma} \rangle^2 q(\vartheta_0, \varphi_0)^2 \alpha^2 \int_{-\infty}^{\infty} U(t)e^{i\alpha t}dt^2
\]

\[
\approx \frac{\theta' \cos^2 \vartheta_0 \cos^2 \varphi_0}{4 \theta' \sinh^2 \left( \frac{\pi \omega}{\alpha \varphi} \right)}.
\]

In Eq. (14), \( q(\vartheta_0, \varphi_0) = \frac{\tan(d \cos \vartheta_0 \cos \varphi_0) \cos \vartheta_0 \cos \varphi_0}{\omega = |E_i - E_f| / \hbar} \) is the average vibrational quantum for the transition \( i \rightarrow f \). \( \theta' = (4 \pi^2 \omega^2 m) / (\alpha^2 k) \), \( \theta = (\hbar \omega) / k \), and \( u = \sqrt{2E/m} \). Note that two different symbols, i.e., \( \vartheta \) and \( \theta \), are being used throughout the paper for the rotation angle and the characteristic vibrational temperature, respectively. The product \( \nu \gamma \) can be interpreted as an effective collision velocity. One can see that at \( \vartheta = \gamma = \varphi = 0 \), one has \( \nu = 1 \), \( E = E_{uu} \), \( q(\vartheta_0, \varphi_0) = 1 \), and Eq. (14) coincides with the one-dimensional probability of the single-quantum transition \( 0 \rightarrow 1 \), predicted by the SSH theory. The difference between the present forced harmonic oscillator—free rotor (FHO-FR) model and the one-dimensional SSH theory result is that Eqs. (10), (12), and (14) incorporate three-dimensional trajectories of rotating molecules as well as the coupling of vibrational states during a collision.

III. COMPARISON WITH TRAJECTORY CALCULATIONS

To verify the accuracy of the present model, it has to be compared with three-dimensional semiclassical trajectory calculations for the atom–diatom collisions, for the potential-energy surface given by Eq. (3). For this purpose, we have used the computer code ADIAV developed by Billing. The code calculates classical translational–rotational collision trajectories and evaluates vibrational transition probabilities by solving a set of coupled equations for the time-dependent expansion coefficients of the vibrational wave function over a basis of stationary states of a molecule. In this section, calculations were made for collisions of an \( N_2 \) molecule and an atom of the same mass of \( m_c = 28 \) amu, so that \( \xi = m/2m_0 = 1 \). The coupling matrix elements \( \langle i | \hat{\gamma} | i \pm 1 \rangle \) used by ADIAV were calculated for the frequency corrected harmonic oscillator (i.e., with harmonic wave functions but anharmonic energy spectrum), with up to 30 states used for the vibrational wave function expansion. The frequency corrected harmonic oscillator approximation also implies that parameter \( \omega \) in the FHO-FR model is evaluated as the average vibrational quantum of a transition, i.e., \( \omega = |E_i - E_f| / \hbar \). The \( N_2 \) vibrational quantum, the anharmonicity, and the equilibrium atom separation were taken to be \( \omega_0 = 2359.6 \) cm\(^{-1} \), \( \omega_0 x_0 = 14.456 \) cm\(^{-1} \), and \( r_0 = 1.094 \) Å. The intermolecular repulsive potential parameters used were \( A = 1730 \) eV, and \( \alpha = 4.0 \) Å\(^{-1} \).

The calculation results are summarized in Figs. 3–9. We emphasize that in the present paper we will always compare the absolute values of the analytic FHO-FR probability and numerical ADIAV probability, respectively, evaluated for two identical potential-energy surfaces. We will also use the one-dimensional, collinear-collision SSH probability

\[ P^{SSH}(E) = \left( \frac{\theta'}{\pi \xi / 4(\theta')} \right) \sinh^2 \left( \frac{\pi \omega}{\alpha \varphi} \right) \]
sion parameters, to the same factor \( P^\text{SSH} \). One can see that the FHO-FR probability peaks at somewhat different value of the rotation angle (\( \theta = 0.76\pi \) instead of \( 0.67\pi \) for the ADIAV probability). However, the maximum probability, which exceeds \( P^\text{SSH} \) by more than two orders of magnitude, is predicted quite accurately. Figure 4 shows the ratio of \( P_{10}(E, \epsilon, y, \varphi)/P^\text{SSH}_{10} \), averaged over the rotation angle \( \varphi \) in the range \( [0, \pi] \), as a function of the angular momentum angle \( \varphi \). In Fig. 4, again, \( E = 10^3 \, \text{cm}^{-1}, \epsilon = 0.2, y = 0 \). This time both the predicted optimum value of \( \varphi = 0 \) and the maximum value of probability, which is about a factor of 20 greater than \( P^\text{SSH}_{10} \), are in good agreement (within 30%) with the ADIAV probability, evaluated for the same collision parameters. The effect of rotational energy of a molecule is demonstrated in Fig. 5. One can see that the ratio \( P_{10}(E, \epsilon, y, \varphi)/P^\text{SSH}_{10} \), averaged over \( \varphi \) at \( E = 10^3 \, \text{cm}^{-1}, \epsilon = 0.2, y = 0, \varphi = 0 \) and shown as a function of \( \epsilon = E_{\text{rot}}/E \), peaks at \( \epsilon = 0.2 \), which is also consistent with predictions of ADIAV. Note that (i) the most efficient value of rotational energy is within the limits of applicability of the FHO-FR model, \( \epsilon \leq \frac{1}{2} \), given by Eq. (11), and (ii) the ADIAV transition probability sharply drops at \( \epsilon \rightarrow 1 \), as has been discussed in Sec. II. The last result justifies neglecting rapidly rotating molecule collisions (see Sec. II). Note that the observed decrease of the analytic FHO-FR probability at \( \epsilon \rightarrow 1 \) is merely an artifact since the assumption of the slow rotation is no longer valid at these conditions. However, this behavior simplifies the formal analytic integration over the rotational energies, when necessary. Finally, in Fig. 6, the ratio \( P_{10}(E, \epsilon, y, \varphi)/P^\text{SSH}_{10} \), averaged over \( \varphi \) at \( E = 10^3 \, \text{cm}^{-1}, \epsilon = 0.2, \varphi = 0 \) is plotted versus the impact parameter \( b \). In this case, again, the optimum value of the impact parameter, \( b = 0 \), and the maximum value of the probability agree well.

FIG. 5. Comparison of the analytic FHO-FR probability and the numerical ADIAV probability (both averaged over \( \varphi \)) of the vibrational transition \( 1 \rightarrow 0 \) as a function of the rotational energy of a molecule.

FIG. 6. Comparison of the analytic FHO-FR probability and the numerical ADIAV probability (both averaged over \( \varphi \)) of the vibrational transition \( 1 \rightarrow 0 \) as a function of the impact parameter.

FIG. 7. Comparison of the one-dimensional analytic models (SSH theory and FHO model) with the trajectory calculations by ADIAV.

FIG. 8. Comparison of the three-dimensional FHO-FR transition probabilities with the trajectory calculations by ADIAV for the low-vibrational quantum numbers. The FHO-FR probability of Eqs. (10), (12), and (14) is numerically averaged over the collision parameters \( \vartheta, \varphi, \epsilon, \) and \( y \) [see Eq. (15)].
The respective ADIAV transition probabilities in a collision energy range $E = 10^3 - 10^6 \text{ cm}^{-1}$ were obtained by Monte Carlo averaging over 1000 randomly chosen trajectories with the same value of $E$, which provided 10%-20% accuracy. The initial separation between a molecule and an atom was 15 Å, and the maximum impact parameter was 2.5 Å.

First, we compared the Monte Carlo averaged ADIAV probabilities with two analytic models, both based on one-dimensional collinear-collision trajectories, i.e., the SSH theory\textsuperscript{24} and the FHO model.\textsuperscript{28,29} Figure 7 shows that the predictions of both these models significantly disagree with the trajectory calculations by ADIAV. At the low-collision energies, the agreement might be somewhat improved by introducing a constant corrective steric factor, which is a rather commonly used procedure. However, one can see from Fig. 7 that at high-collision energies, both these models completely break down. It is not surprising that the SSH theory fails because it is based on first-order perturbation theory and cannot be used for calculations of large transition probabilities. The only reason for the breakdown of the non-perturbative FHO model, however, is that it does not consider realistic three-dimensional collision trajectories. Indeed, the FHO model predicts a sharp decrease of the probabilities at high energies. However, even if the collision energy is large, there are always some configurations of the collision parameters, $\epsilon, \gamma, \theta$, and $\varphi$, for which the parameter $\gamma$ in Eqs. (10) and (14) is small (e.g., for $\epsilon \sim 0$ and $\gamma \sim 1$, $\gamma \sim 0$). For these configurations, the effective collision velocity in Eq. (14), $u \gamma$, is much smaller and, therefore, the transition probability is much greater. For this reason the incorporation of three-dimensional trajectories into the FHO model, carried out in Sec. II, is expected to diminish or even completely remove the probability drop at high-collision energies, thereby improving the agreement with the trajectory calculations.

This qualitative conclusion is confirmed by Fig. 8 which compares the three-dimensional FHO-FR transition probabilities $P_{10}$, using the same FHO scaling law of Eq. (12), with the trajectory calculations by ADIAV. One can see the remarkable agreement in the entire collision energy range considered, both for single-quantum and multiquantum processes, up to $s = 5$. Further calculations showed that the FHO-FR model accurately predicts the probabilities of the processes where as many as 10 quanta are transmitted. Beyond this point running ADIAV for a large number of trajectories ($N \sim 10^3$) becomes fairly time consuming because of the increasing number of coupled equations involved (50--60 for $s = 10$). Figure 9 also demonstrates that the agreement is also very good even for high-vibrational quantum numbers, $i \sim 40$. In particular, this proves that the FHO scaling law of Eq. (12), developed for harmonic oscillator, is also quite accurate for the frequency corrected oscillator used in the present calculations by ADIAV.

Note that the approximation $(R^2 + r^2)^{1/2} / (R + r \cos \theta)^{1/2}$, used to derive Eq. (3) becomes rather crude
for collision energies $E \sim 10^5 \text{ cm}^{-1}$. On the other hand, trajectory calculations by ADIVAV without using this approximation still show very little difference from the approximate analytic model even at $E \sim 10^6 \text{ cm}^{-1}$. In addition, collisions with energies $E > 10^5 \text{ cm}^{-1}$ affect the thermally averaged relaxation rates only at extremely high temperatures, $T > 10^3 \text{ K}$.

The results of the model validation calculations discussed above demonstrate that the analytic FHO-FR formulas given by Eqs. (10), (12), and (14) accurately predict the transition probability dependence on all collision parameters such as total energy, molecular orientation during the collision, rotational energy, and impact parameter. The model is applicable in a very wide range of collision energies and vibrational quantum numbers, as well as for processes of transfer of many vibrational quanta. The last result also allows using the FHO-FR model for the accurate prediction of the rates of molecular dissociation from low-vibrational levels by a single collision. Thus, taking into account (i) modulation of the interaction potential by the molecular rotation which is assumed to be free, (ii) nonzero impact parameters collisions using the modified wave number approximation, and (iii) many-state coupling using the FHO model, permits capturing the principal mechanism of molecule-to-atom vibrational energy transfer and gives an accurate three-dimensional analytic rate model.

**IV. AVERAGING THE PROBABILITIES AND DISCUSSION**

To make the FHO-FR model useful for practical calculations, we have to find the transition probabilities as functions of only total collision energy $E$, that is to analytically evaluate the integral of Eq. (15). This integral can be calculated by the steepest descent method. First, let us rewrite Eq. (14) as follows:

$$Q^e(E, \epsilon, \gamma, \theta, \phi) = \frac{\theta^e \xi^2}{\theta} \exp \left[ 2s \cdot \ln(\cos \theta \cos \varphi) - \frac{2 \pi \omega s}{\alpha \epsilon} \right]$$

$$= \frac{\theta^e \xi^2}{\theta} \exp \left[ G(\epsilon, \gamma, \theta, \phi) \right].$$

The approximation $\sinh(\chi) \approx \chi^2/2$ made in Eq. (16) is very accurate except for very high-collision energies such that $\chi = \pi \omega \xi \alpha \epsilon \gamma \approx 1$. Second, from Eqs. (10), (12), and (16) we have to determine the optimum configuration of parameters $\epsilon, \gamma, \theta, \phi$, for which the probability $P_i^f$ of Eq. (12) reaches maximum at a given total energy $E$. One can see that if $Q \approx s_{th}$, such as

$$s_{th} = \frac{(s+1)(s+2)}{2n_s} \left( \sqrt{\frac{3s+2}{s+2}} - 1 \right),$$

this occurs when both $Q$ in Eq. (12) and $G \sim s \cdot \ln Q$ in Eq. (16) are maximum. If $Q$ can exceed $s_{th}$, $P_i^f$ always reaches maximum at some $Q^* \approx s_{th}$ such as $Q^* = s_{th}$. The superscript \( \ast \) will denote the optimum configuration parameters through the remainder of this paper.

If $Q \leq s_{th}$, the unique optimum configuration is

$$\cos^2 \theta^* = \begin{cases} 1 + \sqrt{1 + 8a}, & \frac{\alpha \omega}{\xi} \xi \geq 1, \\ 1, & a < 1 \end{cases},$$

$$\phi^* = 0; \quad \gamma^* = 0; \quad \epsilon^* = \frac{\xi \sin^2 2q^*}{4 + \xi \sin^2 2q^*},$$

$$\gamma^* = \sqrt{1 + \xi \sin^2 2q^*/4}. \quad (18)$$

To avoid cumbersome calculations, from now on we will concentrate on a separate analysis of the two specific cases of Eq. (18), first corresponding to the collisions of a molecule with a heavy atom ($\xi = m/2m_0 \approx 1$), such as $N_2$–Ar

$$\theta^* = \frac{3 \pi}{4}; \quad \varphi^* = 0; \quad \gamma^* = 0; \quad \epsilon^* = \frac{\xi}{4 + \xi};$$

and second that applies to the collisions of a molecule with a light atom ($\xi = m/2m_0 \ll 1$), such as $N_2$–He

$$\theta^* = 0; \quad \varphi^* = 0; \quad \gamma^* = 0; \quad \epsilon^* = 1;$$

$$\gamma^* = \sqrt{1 + \xi \sin^2 2q^*/4}. \quad (18a)$$

At the same collision energy, the values of parameter $a = \pi \omega \xi \alpha \epsilon$ for these two cases differ by about a factor of 10, being $a = 33.6$ and $a = 3.3$ at $E = 10^5 \text{ cm}^{-1}$, respectively. One can see both the similarities and the qualitative difference between these two cases. In both cases, zero impact parameter collisions ($\gamma^* = 0$) are most efficient for the vibrational energy transfer. However, in the first case the probability reaches maximum for a noncollinear collision ($\theta^* = 3 \pi/4$) of a rotating diatomic molecule ($\epsilon^* = E_{rot}/E = 0.2$ for $\xi = 1$) with an atom, when the angular momentum vector is perpendicular to the radius vector $R$ near the point of maximum interaction ($\varphi^* = 0$, see Fig. 1). On the other hand, in the second case the most efficient configuration is a head-on collision of a nonrotating molecule. The maximum probability for these two optimum configurations, $P_i^f$, is given by Eq. (12), where now

$$Q^* = \frac{1}{2} \cos^2 \theta \exp \left[ - \frac{2 \pi \omega \xi}{\alpha \epsilon \sqrt{1 + \xi^2/4}} \right]. \quad (19a)$$

and

$$Q^* = \frac{\theta \xi^2}{\alpha \epsilon} \exp \left[ - \frac{2 \pi \omega \xi}{\alpha \epsilon} \right]. \quad (19b)$$

respectively.

Expanding the probability of Eq. (12) in a series near the optimum configuration point $\epsilon^*, \gamma^*, \varphi^*, \phi^*$, for the two cases described by Eqs. (18a) and (18b), and formally extending the integration limits to infinity, one obtains for $Q \leq s_{th}$
\[ P_{if}(E, Q \ll s^*) \approx P_{if}^* \int_{-\infty}^{\infty} e^{G_e^* + 2z^2/\alpha} \, dz \int_{-\infty}^{\infty} e^{G_y^* + 2z^2/\beta} \, dz \int_{-\infty}^{\infty} e^{G_\theta^* + 2z^2/\gamma} \, d\theta \int_{-\infty}^{\infty} e^{G_\phi^* + 2z^2/\delta} \, d\phi \]

\[ = P_{if}^* \sqrt{\frac{\alpha \xi \gamma \delta}{\omega \gamma \delta \epsilon}} \left( \frac{2}{s^{3/2}} \right) \left( \frac{\alpha u}{\pi \omega} \right)^{5/2} \approx 2 P_{if}^* \left( \frac{\alpha u}{\pi \omega} \right)^{5/2} \]  

(20a)

and

\[ P_{if}(E, Q \gg s^*) \approx P_{if} \int_{0}^{\infty} e^{G_e^* + 2z^2/\alpha} \, dz \int_{0}^{\infty} e^{G_y^* + 2z^2/\beta} \, dz \int_{0}^{\infty} e^{G_\theta^* + 2z^2/\gamma} \, d\theta \int_{0}^{\infty} e^{G_\phi^* + 2z^2/\delta} \, d\phi \]

\[ = P_{if} \sqrt{\frac{\alpha \xi \gamma \delta}{\omega \gamma \delta \epsilon}} \left( \frac{2}{s^{3/2}} \right) \left( \frac{\alpha u}{\pi \omega} \right)^{5/2} \approx P_{if} \left( \frac{\alpha u}{\pi \omega} \right)^{5/2} \]  

(20b)

In Eqs. (20a) and (20b), \( \bar{\epsilon} = \epsilon - \epsilon^* \), \( \bar{\gamma} = \gamma - \gamma^* \), \( \bar{\theta} = \theta - \theta^* \), \( \bar{\phi} = \phi - \phi^* \).

For \( Q = s^* \), the maximum value of the probability at the optimum configuration point given by Eqs. (18a) and (18b) is the same both for relaxation by a heavy and by a light atom

\[ P_{if}^* \approx \frac{s^*}{s^!} \exp(-s), \]  

(21)

and expression for the transition probability modifies

\[ P_{if}(E, Q = s^*) \approx P_{if}^* \prod_{i=1}^{s!} \int_{0}^{\infty} e^{(\ln Q - Q/s^*)^2} \, dz \int_{0}^{\infty} e^{(\ln Q - Q/s^*)^2} \, dz \]

\[ = P_{if}^* \left( \frac{\alpha u}{\pi \omega \sqrt{s}} \right) \left( \frac{2}{s^{1/2}} \right) \left( \frac{\alpha u}{\pi \omega \sqrt{s}} \right) \]

\[ \times \left( \frac{\alpha u}{\pi \omega \sqrt{s}} \right) \left( \frac{2}{s^{1/2}} \right) \left( \frac{\alpha u}{\pi \omega \sqrt{s}} \right) \]

\[ = P_{if}^* \left( \frac{\Gamma^2(\frac{1}{4})}{\pi s^{3/2}} \right) \left( \frac{2}{s^{1/2}} \right) \left( \frac{\alpha u}{\pi \omega} \right)^{5/2} \approx 4 P_{if}^* \left( \frac{\alpha u}{\pi \omega} \right)^{5/2} \]  

(22a)

and

\[ P_{if}(E, Q = s^*) \approx P_{if} \prod_{i=1}^{s!} \int_{0}^{\infty} e^{(\ln Q - Q/s^*)^2} \, dz \int_{0}^{\infty} e^{(\ln Q - Q/s^*)^2} \, dz \]

\[ = P_{if} \left( \frac{\alpha u}{\pi \omega \sqrt{s}} \right) \left( \frac{2}{s^{1/2}} \right) \left( \frac{\alpha u}{\pi \omega \sqrt{s}} \right) \]

\[ \times \left( \frac{\alpha u}{\pi \omega \sqrt{s}} \right) \left( \frac{2}{s^{1/2}} \right) \left( \frac{\alpha u}{\pi \omega \sqrt{s}} \right) \]

\[ = P_{if} \left( \frac{\Gamma^2(\frac{1}{4})}{\pi s^{3/2}} \right) \left( \frac{2}{s^{1/2}} \right) \left( \frac{\alpha u}{\pi \omega} \right)^{5/2} \approx 2 P_{if} \left( \frac{\alpha u}{\pi s^{3/2}} \right) \left( \frac{\alpha u}{\pi \omega} \right)^{5/2} \]  

(22b)
One can see that the expressions for the transition probabilities \( P_{if}(E) \) in Eqs. (20) and (22) each contain a product of four factors due to integration over the collision parameters, \( y, \varepsilon, \theta, \) and \( \varphi. \) For modeling of flows with rotational disequilibrium one can also obtain the probabilities as functions of both total collision energy and rotational energy, \( P_{if}(E, \varepsilon) \), by skipping the integration over \( \varepsilon. \) The accuracy of the approximate integration in Eqs. (20) and (22) is 50%-100% compared with numerical integration in Eq. (15). Spreading of the probability maximum near the optimum configuration point is the main reason causing the accuracy to become somewhat worse as the collision energy increases.

If \( Q > s^\text{th} \), the optimum configuration of collision parameters is no longer unique and cannot be found in closed analytic form. However, the asymptotic behavior of the probability at \( Q \gg s^\text{th} \) can be roughly estimated using the following simple argument. At high-collision energies, the multiple optimum configurations are realized at \( Q^* = s^\text{th} \leq Q \) and, therefore, at \( \gamma^* \ll 1. \) Assuming the values of \( \gamma \in [0, \sqrt{1+\xi/4}] \) to be approximately equiprobable, one can write

\[
P_{if}(E, Q) \approx s^\text{th} = P_{if}^* \int_0^\infty e^{\varepsilon/\ln Q - Qs^\text{th} \gamma^*} \gamma^2 d\gamma
\]

\[
= P_{if}^* \frac{1}{\sqrt{s}} \left( \frac{a u \gamma}{\pi \omega} \right)^* = \text{const.}
\] (23)

In Eq. (23), \( \gamma = \gamma - \gamma^* \), \( (au \gamma/\pi \omega)^* \) denote the multiple points where \( Q = Q^* = s^\text{th} \), and \( P_{if}^* \) is given by Eq. (21).

Finally, the following two interpolation formulas bridge the gap between the three specific cases covered by Eqs. (20), (22), and (23) and provide fairly accurate expressions for the transition probabilities in the entire range of collision energies considered, \( E = 10^{-10} \) cm\(^{-1}.\)

\[
P_{if}(E) = \begin{cases} 
2 s^{-5/2 + 5A/4} \left( \frac{a u}{\pi \omega} \right)^{5/2} 
\times \left( n_s \right)^s 
\times \left( \frac{s}{s^!} \right) \exp \left( -2n_s \right) 
\times \left( \frac{2^{1/2} - 3/4A}{2^{1/2} - 3/4A} \right) 
\times \left( \frac{1}{2} \ln \left( \frac{\theta' \xi}{2s^m \theta} \right) \right) 
\times \left( \frac{s}{s^!} \right) \exp (-s), \quad \lambda = \frac{Q^*}{s^m} > 1
\end{cases}
\]

\[
P_{if}(E) = \begin{cases} 
\frac{1}{\pi} s^{-3 + 3A/2} \left( \frac{a u}{\pi \omega} \right)^2 
\times \left( n_s \right)^s 
\times \left( \frac{s}{s^!} \right) \exp \left( -2n_s \right) 
\times \left( \frac{1}{\pi} \right) \left( \frac{s}{s^!} \right) \exp (-s), \quad \lambda = \frac{Q^*}{s^m} > 1
\end{cases}
\] (24a)

In Eqs. (24a) and (24b), factors \( s^\text{th} \) and \( Q^* \) are given by Eqs. (17), (19a), and (19b). Figures (10) and (11) compare the probabilities of Eqs. (24a) and (24b) with the trajectory calculations by ADIAV for collisions of \( \text{N}_2 \) molecule with a heavy atom (Ar) and a light atom (He), respectively. The potential used is the same as in Sec. II. One can see that the accuracy of the analytic probabilities is typically within a factor of 2. Equations (24a) and (24b) can be used in the direct Monte Carlo modeling of strongly nonequilibrium flows of rarefied gases, for example, behind strong bow shocks.\(^{43}\)

Thermally averaged relaxation rate coefficients \( k_{if}(T) \) can be determined by averaging of the transition cross sections over the Boltzmann distribution\(^{42}\)

\[
k_{if}(T) = \langle u \rangle \int_0^\infty \sigma_{if}(E) \exp \left( \frac{E}{T} \right) d\left( \frac{E}{T} \right)
\]

\[
= \pi R_0^2 \langle u \rangle \int_0^\infty \left( \frac{E}{T} \right)^2 P_{if}(E) \exp \left( \frac{E}{T} \right) d\left( \frac{E}{T} \right). \tag{25}
\]
for the cross section appears due to integration over the values of orbital kinetic energy (or orbital angular momentum) and rotational energy (or rotational angular momentum). The maximum interaction distance $R_0$ is found as $U(R_0) = kT$, $R_0 \equiv 2.5 \text{ A}$ at $T \approx 10^4 \text{ K}$. Then the effective cross section for elastic collisions is $\langle \sigma_{el} \rangle = k_{el}(T)/\langle u \rangle = 2\pi R_0^2$, and the gas kinetic collision frequency is $Z = 2\pi R_0^2 \langle u \rangle$.

Evaluation of the integral in Eq. (25) at $Q \leq s^{th}$ yields $k_{ij}(T)$

$$k_{ij}(T) = \pi R_0^2 \langle u \rangle \left( \frac{n_i}{s!} \frac{1}{\sqrt{3} \xi} \frac{\theta^s}{\theta} \right)^{1/2} C_{VT}^{15/2} s^{3/4}$$

$$\times \exp \left[ -\frac{1}{4\theta} \left( \frac{1}{s} \frac{(1 + \xi/4)T}{\theta^s} \right)^{1/3} - s(1 - C_{VT}^{3/4}) \right]$$

$$\times \exp \left[ \frac{\theta s}{2T} \left( 1 - \frac{\theta}{4T} \left( \frac{(1 + \xi/4)T}{\theta^s} \right)^{1/3} \right) \right],$$

$$\lambda = \frac{1}{3} \frac{\theta^s}{\theta} \exp \left[ -1 \frac{1}{C_{VT}} \left( \frac{\theta^s}{\theta^s} \right)^{1/3} \right]$$

and

for the collisions with a heavy and a light atom, respectively. The last exponential factor in Eqs. (26a) and (26b) originates from the symmetrization of collision energy in Eq. (25). Following the procedure suggested in Ref. 42, we evaluate the rates of exothermic processes. The endothermic rates can be found simply as $k_{exo} = k_{el} \exp(-\theta s/T)$. Eqs. (26a) and (26b) are valid only if $T \leq T^th$, where $T^th$ is the threshold temperature that corresponds to the “switching” from the unique to the multiple optimum configuration regime

$$T^th = \frac{15}{2} \left( \frac{1}{s^h \theta} \right)$$

and

$$T^th = \frac{\theta^s}{7 \ln^2 \frac{\theta^s}{s^h \theta}}$$

Factor $C_{VT}$ in Eqs. (26a) and (26b) determines the collision energy at which the integrand in Eq. (25) reaches maximum, and can be found by solving transcendental equations

$$C_{VT} = \left[ 1 - \frac{1}{s^h \theta} \exp \left[ -\theta^s \left( \frac{\theta^s}{\theta^s} \right)^{1/3} \right] \right]$$

and

$$C_{VT} = \left[ 1 - \frac{1}{s^h \theta} \exp \left[ -\theta^s \left( \frac{\theta^s}{\theta^s} \right)^{1/3} \right] \right]$$

respectively. The deviation of $C_{VT}$ from unity characterizes the influence of multistate coupling effects. At small values of $C_{VT}$, we are far from the first-order perturbation limit. Eqs. (28a) and (28b) both have a single root and in practical calculations can be easily solved by the Newton method. From Eq. (28b), one can see that the most efficient dimen-
sionless collision energy decreases with temperature from $\frac{E^*}{kT} = \frac{1}{2} (\theta s^2/T)^{1/3}$ to $\frac{E^*}{kT} = 7/2$ at $T = T^\text{th}$ [a similar relation can be obtained from Eq. (28a)]. In other words, at the high temperatures such as $T > T^\text{th}$, vibrational energy transfer mainly occurs in collisions at nearly thermal energies.

At $Q > s^\text{th}$ (i.e., at $T > T^\text{th}$), the result of integration is

$$k_{ij}(T) = 2\pi R_0^2(u) \frac{s^i}{s^!} \times \exp(-s) \frac{1}{s^{1/2+3/4k}} \left[ \frac{1}{2} \ln \left( \frac{\theta}{2 s^i \theta} \right) \right]^{-1-3/2k} \times \exp \left( \frac{\theta s}{2T} \left[ 1 - \frac{\theta}{30T} \right] \right)$$

$$\lambda^2 = \frac{1}{s^\text{th}} \frac{\theta'}{2 \theta} \exp \left[ - \left( \frac{2 \theta'}{15(1 + \xi/4/T)} \right)^{1/2} \right] \quad (29a)$$

and

$$k_{ij}(T) = 2\pi R_0^2(u) \frac{s^i}{s^!} \times \exp(-s) \frac{1}{s^{1/2+1/2k}} \left[ \frac{1}{2} \ln \left( \frac{\theta}{s \theta} \right) \right]^{-1-1/2k} \times \exp \left( \frac{\theta s}{2T} \left[ 1 - \frac{\theta}{28T} \right] \right)$$

$$\lambda^2 = \frac{1}{s^\text{th}} \frac{\theta'}{\theta} \exp \left[ - \left( \frac{\theta'}{7T} \right)^{1/2} \right] \quad (29b)$$

From Eqs. (29a) and (29b), one can see that the asymptotic behavior of the rate coefficients at $T > T^\text{th}$ is $k_{ij}(T) \sim \text{const} \cdot Z$. This again shows that the use of steric factors with the available one-dimensional rate models at high temperatures is completely erroneous (see also Fig. 7).

At low temperatures, such as $T \ll T^\text{th}$, one has $C_{VT} \approx 1$, and the expressions for the relaxation rates simplify

$$k_{ij}(T) = 2\pi R_0^2(u) \frac{(n_s)^i}{(s^!)^2} \frac{4(1 + \xi/4)}{\sqrt{3\xi}} \left( \frac{\theta'}{2 \theta} \right)^s \times \exp \left\{ \frac{3}{2} \left( \frac{\theta'}{1 + \xi/4/T} \right)^{1/3} \right\} \times \exp \left( \frac{\theta s}{2T} \left[ 1 - \frac{\theta}{4T} \left( \frac{1 + \xi/4/T}{\theta' s^2} \right)^{1/3} \right] \right\}$$

$$\lambda^2 = \frac{1}{s^\text{th}} \frac{\theta'}{\theta} \exp \left[ - \left( \frac{\theta'}{7T} \right)^{1/2} \right] \quad (30a)$$

and

$$k_{ij}(T) = 2\pi R_0^2(u) \frac{(n_s)^i}{(s^!)^2} \frac{4(1 + \xi/4)}{\sqrt{3\xi}} \left( \frac{\theta'}{2 \theta} \right)^s \times \exp \left\{ \frac{3}{2} \left( \frac{\theta'}{T} \right)^{1/3} \right\} \times \exp \left( \frac{\theta s}{2T} \left[ 1 - \frac{\theta}{4T} \left( \frac{T}{\theta' s^2} \right)^{1/3} \right] \right\}$$

$$\lambda^2 = \frac{1}{s^\text{th}} \frac{\theta'}{\theta} \exp \left[ - \left( \frac{\theta'}{7T} \right)^{1/2} \right] \quad (30b)$$

One can see that at $s = 1$ (for single-quantum processes) the latter equation exactly coincides with the one-dimensional SSH formula with a steric factor of $1/\pi$. This is not surprising since we have already seen that for relaxation by a light atom, the head-on collisions of a nonrotating molecule are the most efficient. In this case the only difference from the one-dimensional theory originates from the non-collinear orientation of a molecule. As is well known, this results in appearance of a $1/3$ steric factor in the SSH formula. However, for the relaxation by a heavy atom, the incorporation of rotation and nonzero impact parameter collisions change both the pre-exponential factor and the exponential dependence of the rate [see Eq. (30a)]. In this case, the one-dimensional SSH formula cannot match either the FHO-FR model or the results of trajectory calculations by using a single temperature-independent steric factor. It is still possible to enforce the agreement between the SSH theory and the three-dimensional models, within a relatively narrow temperature range, by introducing a steric factor and varying the repulsive potential parameter $\alpha$ at the same time. This procedure, however, should be regarded as nothing more than a curve fitting to available three-dimensional data.

The values of the threshold temperature for $O_2$–Ar collisions, given by Eq. (27), change from $T^\text{th} = 9200$ K for the transition $1 \to 0$ to $T^\text{th} = 1400$ K for the transition $30 \to 29$. This shows that both Eq. (26) and Eq. (29) must be used for the high-temperature vibrational relaxation rate calculations. Figures 12 and 13 compare the rates of Eqs. (26) and (29), calculated for $O_2$–Ar at $s = 1$ and $s = 5$, with the trajectory calculations by ADIAV in the temperature range of $200 \leq T \leq 50,000$ K and vibrational quantum number range $0 \leq i \leq 30$, showing satisfactory agreement. In these calculations, $\omega_e = 1580.3$ cm$^{-1}$, $\omega_{ex} = 12.072$ cm$^{-1}$, $r_e = 1.207$ A, and the potential parameters are the same as before, $A = 1730$ eV, and $\alpha = 4.0$ A$^{-1}$.

Up to this point, both analytic and numerical calculations have been made for the frequency corrected harmonic
oscillator (HO), i.e., assuming coupling only between the adjacent quantum states, \( i \) and \( i \pm 1 \), and the simple purely repulsive potential of Eq. (3). To evaluate the effect of anharmonic nonadjacent state coupling on the relaxation rates, an additional series of calculations by ADIAV was made, using the Morse oscillator (MO) coupling matrix elements, \( \langle i \mid P \mid i \pm s \rangle \) \((s \leq 3)\). It was found that the anharmonic coupling affects the rate \( k_{10}(T) \) fairly weakly, the ratio \( k_{10,\text{MO}} / k_{10,\text{HO}} \) being less than a factor of 2 even at \( T \sim 10^4 \) K. Finally, we compared the FHO-FR model predictions for \( \text{N}_2-\text{He} \) relaxation rates with the numerical calculations by ADIAV using \text{ab initio} CEPA potential-energy surface,\(^44\) rather than the simplified atom-to-atom potential of Eq. (3). In the present paper, we simply extended the \( \text{N}_2-\text{He} \) ADIAV-CEPA calculations\(^45\) toward the high-collision energies. Analytic FHO-FR relaxation rates have been evaluated using the value of \( \alpha = 4.0 \) A\(^{-1}\), obtained by the least-squares fit of Eq. (3) to the CEPA potential. The results, shown in Fig. 14, again demonstrate very good agreement between the trajectory calculations and the analytic model. Note that the long-range attractive part of the CEPA potential (with the maximum well depth of 17 K) significantly affects the rates only below room temperature (see Fig. 14). At 300 K, the difference between the ADIAV-CEPA and the FHO-FR rates does not exceed a factor of 2, and even at \( T = 100 \) K the difference is about a factor of 3 (see Fig. 15). Also shown in Figs. 14 and 15 are the low-temperature experimental measurements of \( k_{10} \).\(^46\)

Both results demonstrate that the approximation of a purely repulsive interaction of a frequency corrected harmonic oscillator and an atom is reasonably accurate within a wide temperature range. Therefore, the state-specific rate coefficients of Eqs. (26) and (29) can be used in kinetic modeling calculations both at near room temperature (such as in gas discharges) and at very high temperatures (e.g., behind shock waves). Note that the repulsive potential parameter \( \alpha \) in each case should be chosen from the best fit of the analytic potential to available experimental and \text{ab initio} data rather than arbitrarily adjusted.

V. SUMMARY

Analysis of classical trajectories of a free-rotating symmetric diatomic molecule acted upon by a repulsive potential allow developing a three-dimensional semiclassical nonperturbative analytic model of vibrational energy transfer in atom–molecule collisions (FHO-FR model). The model takes into account the following coupled effects: (i) Interaction potential modulation by free rotation of an arbitrarily oriented molecule during a collision, (ii) reduction of the effective collision velocity in nonzero impact parameter collisions of a rotating molecule, and (iii) multistate coupling in a collision.

FIG. 13. Comparison of the thermally averaged FHO-FR rate coefficients of Eqs. (26a) and (30a) with the trajectory calculations by ADIAV for \( \text{O}_2-\text{Ar} \) (multiquantum transitions, \( s = 5 \)).

FIG. 14. Comparison of the FHO-FR rate coefficients with the trajectory calculations by ADIAV using the \text{ab initio} CEPA potential-energy surface for \( \text{N}_2-\text{He} \) (Ref. 44), and with the experiment (Ref. 46). FHO-FR probability of Eqs. (10), (12), and (14) is numerically averaged over the collision parameters \( \vartheta, \varphi, \epsilon, y, \) and \( E \).

FIG. 15. Comparison of the FHO-FR rate coefficients with the ADIAV-CEPA calculations and experimental data (Ref. 46) at the low temperatures.
The FHO-FR model predictions have been compared with close-coupled semiclassical trajectory calculations using the same potential-energy surface. The comparison demonstrates not only very good agreement between the analytic and numerical probabilities across a wide range of collision energies, but also shows that the analytic model correctly reproduces the probability dependence on other collision parameters such as rotation angle, angular momentum angle, rotational energy, impact parameter, and collision reduced mass. The model predicts, equally well, the cross-sections of single-quantum and multiquantum transitions and is applicable up to very high-collision energies and quantum numbers. The resultant analytic expressions for the probabilities do not contain any arbitrary adjustable parameters commonly referred to as steric factors. Additional calculations showed that the effect of anharmonic state coupling is weak, while the influence of attractive forces become substantial only at temperatures $T \lesssim 300$ K. Therefore, the predictions of the model are also applicable at near room temperature. The results obtained in the present paper can be used for calculations of the state-specific relaxation rates of symmetric or nearly symmetric molecules such as N$_2$, O$_2$, and CO, on inert gas atoms such as Ar and He. It remains an open question, however, whether the approach used here is applicable for calculations of vibrational energy-transfer rates in molecule–molecule collisions, in particular for processes induced by long-range multipole–multipole attraction.

The FHO-FR model provides new insight into kinetics of vibrational energy transfer. Analytic expressions for state-specific transitions probabilities and rate coefficients, obtained in the paper, are available from the authors upon request as concise FORTRAN subroutines, which allow their incorporation in existing kinetic models and their use in modeling calculations.

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