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Nima Ghaderi

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Bimolecular recombination reactions: *K*-adiabatic and *K*-active forms of the bimolecular master equations and analytic solutions

Nima Ghaderi

Noyes Laboratory of Chemical Physics, California Institute of Technology, 1200 E. California Blvd., Pasadena, California 91125, USA

Expressions for a K-adiabatic master equation for a bimolecular recombination rate constant k_{rec} are derived for a bimolecular reaction forming a complex with a single well or complexes with multiple well, where K is the component of the total angular momentum along the axis of least moment of inertia of the recombination product. The K-active master equation is also considered. The exact analytic solutions, i.e., the K-adiabatic and K-active steady-state population distribution function of reactive complexes, $g(EJK)$ and $g(EJ)$, respectively, are derived for the K-adiabatic and K-active master equation cases using properties of inhomogeneous integral equations (Fredholm type). The solutions accommodate arbitrary intermolecular energy transfer models, e.g., the single exponential, double exponential, Gaussian, step-ladder, and near-singularity models. At the high pressure limit, the k_{rec} for both the K-adiabatic and K-active master equations reduce, respectively, to the K-adiabatic and K-active bimolecular Rice–Ramsperger–Kassel–Marcus theory (high pressure limit expressions). Ozone and its formation from O + O$_2$ are known to exhibit an adiabatic K. The ratio of the K-adiabatic to the K-active recombination rate constants for ozone formation at the high pressure limit is calculated to be ~0.9 at 300 K. Results on the temperature and pressure dependence of the recombination rate constants and populations of O$_3$ will be presented elsewhere. © *2016 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4944082]

I. INTRODUCTION

Many important bimolecular reactions in the gas phase involve the initial formation of a long lived intermediate. Upon its metastable formation, the intermediate may be collisionally stabilized with a bath gas leading to a stable product, or it may undergo dissociation to reactants,[1–3] in which are amenable to be studied by master equations. In the atmosphere, the principle buffer gases are N$_2$ and O$_2$, where N$_2$ has been noted to be practically inert, while O$_2$ may react readily with various free radical species, e.g., O$_2$ reacting with acetyl radical to produce peroxyacetyl radical in the troposphere,[4] though, a bimolecular reaction involving acetylperoxyl radicals and O$_2$ has been reported to produce OH radicals independent of pressure in pure O$_2$,[5] and thereafter investigated with an energy resolved master equation.[6] In the atmosphere or in other chemical systems, the buffer gas may react with the vibrationally excited species, as well as deactivate it, and such processes may also be investigated by master equations.[6]

The usual treatments of master equations for studying a unimolecular or bimolecular process utilize either an eigenvalue method[1,7–10] or a stochastic based approach,[6,11–14] for obtaining a unimolecular dissociation rate constant k_{uni} or bimolecular recombination rate constant k_{rec} using detailed balance. Presently, both methods are available for the K-active case, where K is the component of the total angular momentum along the axis of least moment of inertia of the recombination product. When K is a dynamically slow variable and shares energy less freely with the remaining relevant degrees of freedom, then it is referred to as K-adiabatic, in contrast to

the K-active case whereby the Coriolis coupling may mix the possible $(2J + 1)$ K levels for the J quantum numbers.[15–17] The ozone molecule is an example of such a system where its K has been investigated to exhibit adiabaticity,[15,18–20] e.g., the role of K in the intermolecular energy transfer with a bath gas,[18] K-diffusion in the metastable ozone,[19,20] and its role in the recombination rate constant for O + O$_2$ → O$_3$ whereby a K-active form of Rice–Ramsperger–Kassel–Marcus (RRKM) theory yielded a k_{rec} for O$_3$ to be greater than a factor of ~2 compared to the K-adiabatic k_{rec}.[15] Comparison of various alternative combinations for the treatment of angular momentum in RRKM theory[16,17] has also been used to investigate Cl + H$_2$O$_2$ association[21] and explored elsewhere.[17] Correspondingly, a K-adiabatic[16,17] formulation of master equation would be relevant and is derived in the present work, along with the K-active[16,17] case for the treatment of angular momenta.

Typically, a k_{rec} as a function of pressure is determined from the detailed balance condition[22–24] $K_{eq} = k_{rec}/k_{uni}$ relating k_{rec} with the k_{uni}, and the equilibrium rate constant K_{eq} relating the reactants A + BC and the molecular product ABC.[25,26] With regards to any "nonequilibrium" aspect[23,24] of the detailed balance condition, it has been observed that when the characteristic time for the internal-energy relaxation is faster than that for a chemical reaction, then phenomenological rate laws may apply, in that duration, with rate coefficients that satisfy the aforementioned detailed balance.[23] Another, ancillary, consideration on selecting to determine k_{rec} directly or from the detailed balance condition is the phase space accessibility for a unimolecular versus

a bimolecular process.[15] For example, the volume for the density of states ρ for the ozone molecule is ~10% smaller when ρ is determined from a unimolecular process versus a bimolecular process at 298 K, where its physical basis lies upon the presence of quasi-periodic trajectories persisting for a unimolecular process and manifesting in the survival probability of the ozone and for its k_{rec}.[15] The recombination rate constant may also be determined directly, upon using the populations acquired from the analytic solution of the master equation.[27]

In previous works, approximate analytic solutions, distribution functions for populations, for a master equation for a unimolecular process for a strong collision model,[1] and solutions for the low pressure limit unimolecular master equation based on various energy transfer models have been derived for their dissociation rate constants.[1,27,28] In one study, a Wiener-Hopf method was used to derive analytic solutions, considered for the energy transfer part of the master equation.[27] For a bimolecular reaction in discrete matrix form, analytic solutions for populations have been derived.[1]

In the present work, the exact analytic solutions (i.e., populations) are derived for the K-adiabatic and K-active based continuum master equation for a bimolecular process, which includes the dissociation, recombination, and energy transfer steps, considered for a bimolecular recombination rate constant using properties of linear inhomogeneous integral equations[29–32] (Fredholm type[29]). A Fredholm equation of the second kind has the form $f(s) = g(s) - \lambda \int_a^b K(s,t)g(t)dt$, where $g(s)$ is the unknown function, $f(s)$ and the kernel $K(s,t)$ are known, and λ is a parameter.[29–32] Fredholm[29] considered various cases for the solutions of this inhomogeneous linear integral equation, and the investigations were further extended by Hilbert and Schmidt.[29–33] In the present work, the exact analytic solutions of the master equation are derived for an arbitrary intermolecular energy transfer model, which can accommodate models such as single exponential,[1] double exponential,[1,34] Gaussian,[1,35,36] step-ladder,[37–39] and near-singularity.[27] Two well utilized models for intermolecular energy transfer are the exponential[1] and biexponential[1,34] models, where information on intermolecular energy transfer in bimolecular reactions has been investigated using classical trajectories,[40–42] and fitting rate results from the master equation to experimental reaction rate.[28]
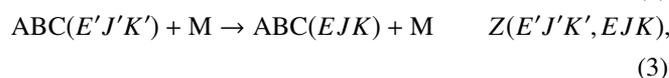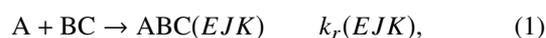
Many important reactions in combustion and atmospheric chemistry may possess intermediate well depths, or combination of deep and shallow wells along the reaction pathway such that the precise time dependence of the populations of reactants, intermediate complexes, and products may be complex.[7,10] In so revealing features of the kinetics, in such situations, tracing the evolution of the time dependence of the populations may be important. In the context of unimolecular theory,[1–3] the two typical approaches to this problem are the lowest-eigenvalue matrix approach[1,7–10] and the stochastic approach,[6,11–14] introduced earlier in this section. In the present paper, recurrence relations[43–45] are also given for the time dependent populations of the K-active and K-adiabatic master equation cases, for single and multiple well and reaction channels.

The paper is organized as follows. In Section II, we derive a K-adiabatic continuum bimolecular master equation for general pressure for a single well and separately for multiple chemical intermediates and reaction channels. In Section III, exact analytic solutions for the populations of reactive complexes are derived for the K-adiabatic and K-active continuum bimolecular master equations (proof provided in Appendix C) for an arbitrary intermolecular energy transfer model, given for a single exponential model and accommodating, e.g., the double exponential, Gaussian, step-ladder, and near-singularity, each noted in Appendix A. The recurrence relations for the time dependence of the K-adiabatic and K-active populations are given in Section IV. The recurrence relation is also considered for finding the energy dependence of the steady-state populations and treated in Appendix B. The discussion is given in Section V, which includes an analytic comparison of the K-active and K-adiabatic populations of the reactive complex and an analytic comparison of the master equations for the recombination rate constants, at the low and high pressure limits. Relevant results on the ozone formation are also noted and discussed. Proof for the reduction of the K-adiabatic and K-active master equations to the high pressure form of the K-adiabatic and K-active RRKM theory, at the high pressure limit, is given in Appendix G. Each Appendix, those above and others, is labeled when noted in a forthcoming section. Summary and concluding remarks are presented in Section VI.

II. THE K-ADIABATIC AND K-ACTIVE BIMOLECULAR RECOMBINATION MASTER EQUATIONS FOR THE GENERAL PRESSURE CASE

A. Single chemical intermediate

The (EJK) resolved kinetic scheme for a bimolecular reaction and energy transfer steps may be described by

$$A + BC \rightarrow ABC(EJK) \qquad k_r(EJK), \qquad (1)$$

$$ABC(EJK) + M \rightarrow ABC(E'J'K') + M \qquad Z(EJK, E'J'K'), \qquad (2)$$

$$ABC(E'J'K') + M \rightarrow ABC(EJK) + M \qquad Z(E'J'K', EJK), \qquad (3)$$

$$ABC(E'J'K') \rightarrow A + BC \qquad k_d^{en}(E'J'K'), \qquad (4)$$

$$ABC(E'J'K') \rightarrow AB + C \qquad k_d^{ex}(E'J'K'), \qquad (5)$$

where A, B, and C are atomic or molecular species, e.g., for simplicity BC may be a diatomic. The *en* and *ex* denote the entrance and the exchange channels, respectively. The $Z(EJK, E'J'K')$ in reaction step 2 is defined as the number of collisions per unit time, per unit energy, with energy transfer between vibrationally and rotationally excited intermediate and a bath gas. The $Z(E'J'K', EJK)$ in reaction step 3 has a similar definition. In a usual procession, a $Z(EJK, E'J'K')$ may comprise the normalized probability of energy transferred with the bath gas, multiplied by the total collision Lennard-Jones frequency, $Z_{LJ} = \omega_{HS}\Omega$, where ω_{HS} is the hard sphere collision frequency and Ω, unitless, is a realistic molecule-bath interaction determined from a collision integral, e.g.,

Lennard-Jones, which corrects the ω_{HS}.[1] Various models for intermolecular energy transfer[1] for the reaction steps 2 and 3 are noted in Appendix A. Reaction steps 1, 4, and 5 may take place only when $E > E^*(JK)$, where $E^*(JK)$ is the critical energy for reaction.

Let $g(EJK)$ be the population density of molecular products ABC (EJK) formed from a process A + BC → ABC, for a given E, J, and K. For an ABC molecule that initially forms from a bimolecular reaction, e.g., reaction step 1, its initial energy is above the dissociation limit, prior to any collision with the bath gas. The equation for the distribution function $g(EJK)$ satisfies the bimolecular master equation

$$\frac{dg(EJK,t)}{dt} = k_r(EJK)A(t) \circ BC(t)$$
$$- g(EJK,t) \sum_{J'K'} \int_{E_o}^{\infty} Z(EJK, E'J'K')dE'$$
$$+ \sum_{J'K'} \int_{E_o}^{\infty} Z(E'J'K', EJK)g(E'J'K',t)dE'$$
$$- k_d(EJK)g(EJK,t) \tag{6}$$

for $E > E^*(JK)$, where the lower limit in the integrals for E' corresponds to the minimum energy of the intermediate, where it may be set to $E_o = -\infty$. The A(t) ∘ BC(t) denotes the concentration of the reactants A and BC, as a function of time. The association rate constant[39] is given by

$$k_r(EJK) = N^*(EJK)e^{-E/kT}/hQ \tag{7}$$

with partition function Q for reactants, and the RRKM theory[1,16,17] dissociation rate constant is given by

$$k_d^{en,ex}(EJK) = N^*(EJK)/h\rho(EJK) \tag{8}$$

for the entrance and exchange channels *en* and *ex*. The $N^*(EJK)$ is the number of states at the transition state (TS),[46] related to the corresponding volume of phase space of the TS, and $\rho(EJK)$ is the density of states of the metastable product. For a process where $E \leq E^*(JK)$, we have instead

$$\frac{dg(EJK,t)}{dt} = -g(EJK,t) \sum_{J'K'} \int_{E_o}^{\infty} Z(EJK, E'J'K')dE'$$
$$+ \sum_{J'K'} \int_{E_o}^{\infty} Z(E'J'K', EJK)g(E'J'K',t)dE', \tag{9}$$

whereupon the dissociation and association channels are now closed, and so each is absent in Eq. (9). A recurrence relation for evolving $g(EJK,t)$ as a function of time, considered for both $E > E^*(JK)$ and $E \leq E^*(JK)$, is given in Section IV.

We next introduce a statistical assumption for the rotational state of ABC after a collision,[1,47]

$$Z(E'J'K', EJK) = P_{eq}(JK|E)Z(E', E), \tag{10}$$

where $P_{eq}(JK|E)$ is the microcanonical equilibrium distribution of J and K for the given E, where we assume a statistical distribution of J and K for any given E of ABC. We write,

similarly,

$$Z(EJK, E'J'K') = P_{eq}(J'K'|E')Z(E, E') \tag{11}$$

and for the steady state approximation, $dg(EJK,t)/dt = 0$, Eq. (6) becomes

$$0 = k_r(EJK)A \circ BC$$
$$- g(EJK) \sum_{J'K'} \int_{E_o}^{\infty} Z(E,E')P_{eq}(J'K'|E')dE'$$
$$+ \sum_{J'K'} \int_{E_o}^{\infty} Z(E',E)P_{eq}(JK|E)g(E'J'K')dE'$$
$$- k_d(EJK)g(EJK). \tag{12}$$

Next factorizing P_{eq} in the second and third terms on the right hand side in Eq. (12) and noting the normalization condition $\int_0^{\infty} P_{eq}dJdK = 1$, then Eq. (12) further simplifies to

$$k_{rec}(EJK)A \circ BC = g(EJK) \int_{E_o}^{\infty} Z(E,E')dE'$$
$$- \sum_{J'K'} \int_{E_o}^{\infty} Z(E',E)g(E'J'K')dE'$$
$$+ k_d(EJK)g(EJK). \tag{13}$$

A K-active $g(EK)$ can be derived following a similar procedure for the K-adiabatic case, except now the K-degree of freedom is not explicitly resolved, or rather assumed to have appropriately been averaged over to yield the K-active master equation, given by[1]

$$k_{rec}(EJ)A \circ BC = g(EJ) \int_{E_o}^{\infty} Z(E,E')dE'$$
$$- \sum_{J'} \int_{E_o}^{\infty} Z(E',E)g(E'J')dE'$$
$$+ k_d(EJ)g(EJ) \tag{14}$$

which is the analogue of Eq. (13).

The analytic solutions, $g(EJK)$ for $E > E^*(JK)$ and $E \leq E^*(JK)$, for Eq. (13) and for its K-active counterpart, Eq. (14), are derived in Section III. The recurrence relations for finding the energy dependence of $g(EJK)$ in Eq. (13) and for the K-active $g(EJ)$ are given in Appendix B.

B. Multiple chemical intermediates

We consider chemical species that can be identified with local minima, wells, on the potential energy hypersurface. For a physical situation with multiple intermediates and reaction channels, the K-adiabatic master equation, Eq. (13), or its K-active counterpart Eq. (14), can be written for each well and the equations then coupled via the chemical reaction terms. Each reaction channel is either associated with another well or with fragmentation products. A master equation describing the time evolution of a population for N distribution functions

$g_i(EJK,t)$, $i = 1, \ldots, N$ for N chemical configurations, of $A \circ BC$ is given by

$$
\begin{aligned}
\frac{dg_i(EJK,t)}{dt} = {} & k_{r_i}(EJK)A(t) \circ BC(t) \\
& - g_i(EJK,t) \sum_{J'K'} \int_{E_o}^{\infty} Z_i(EJK,E'J'K')dE' \\
& + \sum_{J'K'} \int_{E_o}^{\infty} Z_i(E'J'K',EJK)g_i(E'J'K',t)dE' \\
& - \sum_{q \neq i}^{N} k_{iq}(EJK)g_i(EJK,t) \\
& + \sum_{q \neq i}^{N} k_{qi}(EJK)g_q(EJK,t) \\
& - k_{d_i}(EJK)g_i(EJK,t) \\
& - \sum_{p=1}^{n_p} k_{p_i}(EJK)g_i(EJK,t),
\end{aligned}
\tag{15}
$$

where $A(t) \circ BC(t)$ denotes the time dependent bimolecular reactants A and BC, with an association rate constant $k_{r_i}(EJK)$ into well i. The $k_{iq}(EJK)$ is the unimolecular rate coefficient for isomerization from well i to well q, and $k_{qi}(EJK)$ is the rate constant for the reverse process from well q to well i. The $k_{d_i}(EJK)$ is the dissociation rate constant for the i-th chemical intermediate, for well i, dissociating to the original reactants (A and BC); $k_{p_i}(EJK)$ is the analogous dissociation rate constant from well i to a set of bimolecular product p, for n_p product set. The K-active version of Eq. (15) is given by[1,10]

$$
\begin{aligned}
\frac{dg_i(EJ,t)}{dt} = {} & k_{r_i}(EJ)A(t) \circ BC(t) \\
& - g_i(EJ,t) \sum_{J'} \int_{E_o}^{\infty} Z_i(EJ,E'J')dE' \\
& + \sum_{J'} \int_{E_o}^{\infty} Z_i(E'J',EJ)g_i(E'J',t)dE' \\
& - \sum_{q \neq i}^{N} k_{iq}(EJ)g_i(EJ) \\
& + \sum_{q \neq i}^{N} k_{qi}(EJ)g_q(EJ) - k_{d_i}(EJ)g_i(EJK,t) \\
& - \sum_{p=1}^{n_p} k_{p_i}(EJ)g_i(EJ,t),
\end{aligned}
\tag{16}
$$

where all the terms in Eq. (16) are now the K-active counterpart of those defined earlier for Eq. (15). In the usual treatment, the term k_{r_i} appearing in the master equation is rewritten as k_{d_i} and the equilibrium constant K_{eq_i} for $A + BC \rightleftarrows i$ using detailed balance condition.[1] In the present treatment, the k_{r_i} may be retained and determined by using Eq. (7), for each chemical intermediate. Recurrence relations for treating the time evolution of populations are given in Section IV.

III. ANALYTIC SOLUTIONS FOR THE K-ADIABATIC AND K-ACTIVE BIMOLECULAR RECOMBINATION MASTER EQUATIONS

A. K-adiabatic populations $g(EJK)$

We solve Eq. (13) for $g(EJK)$ by recasting Eq. (13) into a form of Fredholm equation and then find its solution in the standard way.[29] Recasting K-adiabatic master equation (13) as a Fredholm of the second kind equation,

$$
y(x) - \lambda \int_a^b k(x,t)y(t)dt = f(x), \quad a \leq x \leq b, \text{ yields}
$$

$$
\begin{aligned}
g(EJK) - \lambda \sum_{J'K'} \int_{E_o}^{\infty} Z(E',E)g(E'J'K')dE' &= f(EJK), \\
E_o \leq E \leq \infty,
\end{aligned}
\tag{17}
$$

where $f(EJK) = 0$ for $E \leq E^*(JK)$, and upon comparing the terms between Eq. (13) and Eq. (17) assists to identify

$$
f(EJK) = \lambda k_r(EJK)A \circ BC
\tag{18}
$$

and

$$
\lambda = \left[\int_{E_o}^{\infty} Z(E,E')dE' + k_d(EJK) \right]^{-1}.
\tag{19}
$$

We seek a solution of the K-adiabatic master equation, Eq. (17), in the form[29–32,48]

$$
g(EJK) = f(EJK) + \lambda \hat{A},
\tag{20}
$$

where $g(EJK)$ is later below partitioned into $g(EJK)_+$ and $g(EJK)_-$ for the energy regions $E > E^*(JK)$ and $E \leq E^*(JK)$, respectively, and the conditions noted for each and the matching boundary condition are given for the populations. The $\hat{A}$ in Eq. (20) is a coefficient determined by substituting $g(EJK)$, Eq. (20), into master equation (17) (steps are delineated in Appendix C) to yield

$$
\hat{A} = \frac{f_1}{[1 - \lambda/\lambda_1]},
\tag{21}
$$

where the identifications are made for

$$
f_1 = \sum_{J'K'} \int_{E_o}^{\infty} Z(E,E')f(E'J'K')dE'
\tag{22}
$$

and

$$
\lambda_1 = \left[\int_{E_o}^{\infty} Z(E,E')dE' \right]^{-1}
\tag{23}
$$

which is a unique characteristic value of Eq. (17), and where λ_1 has been averaged over J' and K'. The integrals in Eq. (21) are supposed to exist, and indeed do on physical grounds, for λ, λ_1, and f_1, when for the latter $k_d \neq 0$ in f_1 for $E > E^*(JK)$ and $f_1 = 0$ for $E \leq E^*(JK)$, and the conditions on λ/λ_1 in Eq. (21) are discussed next and commented in Ref. 49.

On the basis of Eqs. (17)-(23), we obtain the following results regarding the conditions on the solution $g(EJK)$: (1) if $\lambda \neq \lambda_1$[49] (i.e., $E > E^*(JK)$), then for an arbitrary right-hand side of Eq. (17), there exists a unique solution for Eq. (17).

Upon substituting for $f(EJK)$, λ, and $\hat{A}$ into Eq. (20), which can be written in the form

$$g(EJK)_+ = f(EJK) + \frac{\lambda \lambda_1 f_1}{\lambda_1 - \lambda}, \quad E > E^*(JK), \quad (24)$$

is a solution of Eq. (17), where its proof is given in Appendix C. (2) If $\lambda \neq \lambda_1$ and $f_1 = 0$[49] (i.e., $E \leq E^*(JK)$) where the dissociation and recombination events are absent in the master equation but only the energy transfer steps are available (e.g., reaction steps 2 and 3), then a solution of Eq. (17) can be represented in the form

$$g(EJK)_- = \lambda_1 \hat{C}, \quad E \leq E^*(JK), \quad (25)$$

where now $f(EJK) = 0$ in the right hand side of the master equation, Eq. (17), and in Eq. (20), since $k_r(EJK) = 0$ in the numerator of $f(EJK)$, as the associative and dissociative physical processes are absent for $E \leq E^*(JK)$. Eq. (25) is a solution of master equation (12), as confirmed upon its substitution into the master equation, for $E \leq E^*(JK)$ (proof provided in Appendix C), where $\hat{C}$ is a constant to be determined. To determine $\hat{C}$, we utilize the boundary condition,[27] $g(EJK)_- = g_{eq}(EJK)$ when $E \to -D$ (D is the dissociation energy of ABC molecule measured from the bottom of its potential well), where $g_{eq}(EJK)$ denotes the equilibrium probability density that ABC has energy E,

defined by $g_{eq}(EJK) = \rho(EJK)e^{-E/kT}/Q$, where $\rho(EJK)$ is the density of states of the molecule and Q is the partition function of ABC in the center-of-mass system of coordinates. Corrections to the equilibrium density have also been derived for various energy transfer models and is noted here as c_E.[27,28] Writing $g_{eq}(EJK)$ as $g_{eq}(0)e^{-E/kT}$ and equating the latter with $g(EJK)_-$ in Eq. (25), so to be $g_{eq}(0)c_E e^{-E/kT} = \lambda_1 \hat{C}$, and including the c_E, yield for $\hat{C}$,

$$\hat{C} = \frac{g_{eq}(0)c_E e^{-E/kT}}{\lambda_1}, \quad (26)$$

where $\lambda_1 \neq 0$. The following boundary condition holds between the g_+ and g_- domains:

$$\frac{g(EJK)_+}{f(EJK) + \lambda \hat{A}} = \frac{g(EJK)_-}{\lambda_1 \hat{C}} \quad (27)$$

upon noting Eqs. (21) and (24)-(26).[50] Further exposition on the boundary condition is discussed in Appendix D. For the last condition on the solution $g(EJK)$, (3) if $\lambda = \lambda_1$ and $f_1 \neq 0$, then there are no solutions to the master equation.[51] Cases (1) and (2) are focused upon and further treated in the present paper for their interesting physical relevance.

Upon considering case (1), the $E > E^*(JK)$ region, and inserting the expressions for $f(EJK)$, λ, and λ_1, Eqs. (18), (19), and (23), respectively, into $g(EJK)_+$, Eq. (24), then yields

$$g(EJK)_+ = k_r(EJK)A \circ BC / \left[\int_{E_o}^{\infty} Z(E,E')dE' + k_d(EJK) \right]$$

$$+ \frac{\left[\int_{E_o}^{\infty} Z(E,E')dE' + k_d(EJK) \right]^{-1} \left[\int_{E_o}^{\infty} Z(E,E')dE' \right]^{-1} \sum_{J'K'} \int_{E_o}^{\infty} f(E'J'K')Z(E,E')dE'}{\left[\int_{E_o}^{\infty} Z(E,E')dE' \right]^{-1} - \left[\int_{E_o}^{\infty} Z(E,E')dE' + k_d(EJK) \right]^{-1}}. \quad (28)$$

The transition probability $Z(E,E')$ in Eq. (28) satisfies the completeness requirement[52–54] in the form $\int_{-\infty}^{E} Z(E,E')dE'$ $+ \int_{E}^{\infty} Z(E,E')dE' = Z_{LJ}$, where the lower integration limit on the first integral was extended to $-\infty$ for mathematical convenience and the unity was multiplied by the Z_{LJ}. Upon considering both the up and down energy transitions, then $\int_{E_o}^{\infty} Z(E,E')dE'$ may be set to Z_{LJ} in Eq. (28), where $Z(E,E')$ is assumed normalized, multiplied by the Lennard-Jones frequency. Eq. (28) then reduces, also upon rearranging it, to

$$g(EJK)_+ = \frac{k_r(EJK)A \circ BC}{Z_{LJ} + k_d(EJK)}$$

$$+ k_d(EJK)^{-1} \sum_{J'K'} \int_{E_o}^{\infty} f(E'J'K')Z(E,E')dE'. \quad (29)$$

On checking the upper limiting value of $g(EJK)_+$, in the region $E > E^*(JK)$, away from the reaction threshold as energy increases, we find as $E \to \infty$, $[Z_{LJ} + k_d(EJK)]$ $> k_r(EJK)$, since the collision frequency via Z_{LJ} increases, and $k_r \to 0$ according to Eq. (7), so the first term and, similarly, the second term approach zero in Eq. (29), hence $g(EJK)_+ \to 0$ as expected.

We now consider case (2), $E \leq E^*(JK)$, for $g(EJK)_-$. Upon substituting for λ_1 and $\hat{C}$, Eqs. (23) and (26), respectively, into Eq. (25) for $g(EJK)_-$ yields

$$g(EJK)_- = g_{eq}(0)c_E e^{-E/kT} \quad (30)$$

to be the equilibrium distribution of populations multiplied by a correction factor c_E given elsewhere for a single exponential, double exponential, and near singularity models for intermolecular energy transfer.[27,28]

For the single exponential model for intermolecular energy transfer,[1] we have

$$Z(E,E') = \begin{cases} Z_o e^{-(E-E')/\gamma}, & E' < E \\ Z_o e^{-(E'-E)/\gamma'}, & E' > E \end{cases}, \quad (31)$$

where γ and γ' are the deactivation and activation constants, in which they are related to each other by detailed balance. The Z_o contains the normalization constant, $1/(\gamma + \gamma')$, for the transition probability of single exponential model and the Lennard-Jones frequency. For the convenience of the reader, the functional forms of $Z(E,E')$ for other intermolecular energy transfer models, e.g., double exponential, Gaussian, step-ladder, and near singularity models, are given in Appendix A. For the region $E > E^*(JK)$, upon making the substitution for $f(E'J'K')$ and $Z(E,E')$ from Eqs. (18) and (31), into Eq. (29) yields

$$g(EJK)_+ = \frac{k_r(EJK)A \circ BC}{Z_{LJ} + k_d(EJK)} + k_d(EJK)^{-1} Z_o$$
$$\times \sum_{J'K'} \int_{E_o}^{\infty} \frac{k_r(E'J'K') A \circ BC \, e^{-|E-E'|/\gamma^{(')}} dE'}{[Z_{LJ} + k_d(E'J'K')]},$$
$$E > E^*(JK). \quad (32)$$

When the concentration of the reactants $A \circ BC$ is deemed independent of E', e.g., when the concentration of reactants produced in reaction step 4 of the kinetic scheme, with energy E', is negligible compared to the starting initial concentration of reactants, then for simplicity, $A \circ BC$ may be factored outside of the integral sign in the second term of Eq. (32). Likewise, the prime appearing in $k_r(E'J'K')$ for E' may be dropped, and as well the primes on $J'K'$ (again when making the assumption of negligible populations from the counterpart primed channels relative to a dominating reaction step 1), in the second term under the integral sign. For the evaluation of the integral in the second term of Eq. (32), the conditions from Eq. (31) are observed for the energy regions, where $\gamma^{(')}$ in Eq. (32) denotes either selecting γ for the region $E' < E$, or selecting γ' for $E' > E$, with the appropriate limits of integration for each region,[55] and with k_r and k_d defined by Eqs. (7) and (8), respectively. Eq. (32) was derived under the consideration of both the up and down intermolecular energy transfers.

The number of states N^* at the TS that appears in the terms k_r and k_d in Eq. (32) may be determined using variational RRKM theory.[16,17] For example, for a two state TS, the $N^*(EJK)_{eff} = N_{EJK}^{*1} N_{EJK}^{*2} / [N_{EJK}^{*1} + N_{EJK}^{*2} - N_{EJK}^{*1} N_{EJK}^{*2} / N_{EJK}^{max}]$ where N_{EJK}^{*1} and N_{EJK}^{*2} represent the number of states at the two minima in a plot of $N(EJK)$ vs the reaction coordinate R, and N_{EJK}^{max} represents the maximum in the number of states in between these two minima.[15,56–59]

A system of integral equations, e.g., analogue of Eq. (17), may be transformed into a single integral equation (Appendix E), and its analytic solution for populations are given in Appendix F, for a simpler non-isomerizing case.

B. *K*-active populations for *g(EJ)*

The *K*-active counterpart of $g(EJK)$ is

$$g(EJ)_+ = \frac{k_r(EJ)A \circ BC}{Z_{LJ} + k_d(EJ)} + k_d(EJ)^{-1}$$
$$\times \sum_{J'} \int_{E_o}^{\infty} f(E'J')Z(E,E')dE', \quad E > E^*(J), \quad (33)$$

where in the derivation the *K* degree of freedom was averaged over at the outset. Likewise for region $E \leq E^*(J)$,

$$g(EJ)_- = g_{eq}(0)c_E e^{-E/kT}, \quad E \leq E^*(J) \quad (34)$$

is acquired.

IV. RECURRENCE RELATIONS FOR THE TIME DEPENDENT *K*-ADIABATIC AND *K*-ACTIVE BIMOLECULAR MASTER EQUATIONS

A. Single chemical intermediate

We consider the time dependent bimolecular *K*-adiabatic master equation given by Eq. (6), for a single chemical intermediate. In its discretized form with respect to time, Eq. (6) becomes

$$g(EJK, t_{j+1}) = k_r(EJK)A(t_j) \circ BC(t_j)\Delta t$$
$$- g(EJK, t_j)\Delta t \sum_{J'K'} \int_{E_o}^{\infty} Z(EJK, E'J'K')dE'$$
$$+ \Delta t \sum_{J'K'} \int_{E_o}^{\infty} Z(E'J'K', EJK)g(E'J'K', t_j)dE'$$
$$- k_d(EJK)g(EJK, t_j)\Delta t + g(EJK, t_j), \quad (35)$$

where a constant integration step Δt may be chosen and consider a discrete set of points $t_j = \Delta t(j - 1)$, where $j = 1, \ldots, m$, where m is the final time step. Recurrent relation, Eq. (35), may be considered for the separate cases $g(EJK, t_{j+1})_+$ and $g(EJK, t_{j+1})_-$ for the energy regions $E > E^*(JK)$ and $E \leq E^*(JK)$, respectively. When $E \leq E^*(JK)$, then the first and the fourth terms in the right hand side of Eq. (35) are zero since $k_r = 0$ and $k_d = 0$, and the recurrence relation then corresponds as an analog of the continuum master equation, Eq. (9).

For the initial step, $i = 1$, either $g(EJK, t_{j+1})_+$ or $g(EJK, t_{j+1})_-$ may be considered, where the initial conditions are either known, or when suitable, may be selected according to either Eq. (29) or (30) for the steady state solutions and inserted into the right hand side of Eq. (35), along with the remaining functions appearing there,[60] and so one evaluates for the left hand side of Eq. (35). For steps $j \geq 2$, a newly acquired left hand side of Eq. (35) is reinserted back into the right hand side of Eq. (35), so to acquire either $g(EJK, t_{j+1})_+$ or $g(EJK, t_{j+1})_-$ for a desired step t_{j+1}. The $g(EJK, t_{j+1})$'s may be calculated according to a specific intermolecular energy transfer model, such as those appearing in Appendix A. The above protocol then accomplishes evolving the states $g(EJK, t_{j+1})$.

For the selection of the initial condition, if based on a steady state population, the assumption such that an initial transient incubation time has elapsed for the reaction of interest needs to be substantiated, and then the time evolution of $g(EJK, t_{j+1})$ may be calculated in the above treatment. Some problems of interest commensurable to this treatment may involve the study of the evolution of populations on scales longer than the initial transient state, which may include branching factors in the chemical reaction.

The recurrence relation for $g(EJ, t)$ for the K-active counterpart of Eq. (35) is given by

$$g(EJ, t_{j+1}) = k_r(EJ)A(t_j) \circ BC(t_j)\Delta t$$
$$- g(EJ, t_j)\Delta t \sum_{J'} \int_{E_o}^{\infty} Z(EJ, E'J')dE'$$
$$+ \Delta t \sum_{J'} \int_{E_o}^{\infty} Z(E'J', EJ)g(E'J', t_j)dE'$$
$$- k_d(EJ)g(EJ, t_j)\Delta t + g(EJ, t_j), \qquad (36)$$

where the K degree of freedom has appropriately been averaged over. The $g(EJ, t_{j+1})$ may be evolved in a similar fashion as was described for the K-adiabatic case. The recurrence relations for the steady-state solutions to the K-adiabatic and K-active master equation are given in Appendix B.

B. Multiple chemical intermediates

The time-dependent K-adiabatic and K-active master equations describing multiple chemical intermediates and reaction channels were given by Eqs. (15) and (16), respectively. In discretized form, the K-adiabatic master equation, Eq. (15), becomes

$$g_i(EJK, t_{j+1}) = \Delta t \, k_{r_i}(EJK)A(t_j) \circ BC(t_j)$$
$$- g_i(EJK, t_j)\Delta t \sum_{J'K'} \int_{E_o}^{\infty} Z(EJK, E'J'K')dE'$$
$$+ \Delta t \sum_{J'K'} \int_{E_o}^{\infty} Z(E'J'K', EJK)g_i(E'J'K', t_j)dE'$$
$$- \Delta t \sum_{q \neq i}^{N} k_{iq}(EJK)g_i(EJK, t_j)$$
$$+ \Delta t \sum_{q \neq i}^{N} k_{qi}(EJK)g_q(EJK, t_j)$$
$$- \Delta t \, k_{d_i}(EJK)g_i(EJK, t_j)$$
$$- \Delta t \sum_{p=1}^{n_P} k_{p_i}(EJK)g_i(EJK, t_j) + g_i(EJK, t_j)$$
$$(37)$$

for the population distribution functions $g_i(EJK, t), i = 1, \ldots, N$ for N chemical intermediates, and again choosing the nodes for time t_j, $j = 1, \ldots, m$, where m is the final time

step, with a constant integration step Δt, in Eq. (37), and the remaining terms were defined earlier following Eq. (15).

Similarly, the recurrence relation for the time dependent K-active master equation, Eq. (16), is given by

$$g_i(EJ, t_{j+1}) = \Delta t \, k_{r_i}(EJ)A(t_j) \circ BC(t_j)$$
$$- g_i(EJ, t_j)\Delta t \sum_{J'} \int_{E_o}^{\infty} Z(EJ, E'J')dE'$$
$$+ \Delta t \sum_{J'} \int_{E_o}^{\infty} Z(E'J', EJ)g_i(E'J', t_j)dE'$$
$$- \Delta t \sum_{q \neq i}^{n} k_{iq}(EJ)g_i(EJ, t_j)$$
$$+ \Delta t \sum_{q \neq i}^{n} k_{qi}(EJ)g_q(EJ, t_j)$$
$$- \Delta t \, k_{d_i}(EJ)g_i(EJ, t_j)$$
$$- \Delta t \sum_{p=1}^{n_P} k_{p_i}(EJ)g_i(EJ, t_j) + g_i(EJ, t_j), \qquad (38)$$

where the K degree of freedom has been averaged over.

V. DISCUSSION

A. Comments on K

The angular momentum component K in a molecule varies because of Coriolis coupling in the vibrations, coupling, for example, the symmetric and antisymmetric stretching vibrations, about 60 cm^{-1} apart, for ozone at the lowest ozone energies.[15] A K degree of freedom for a given chemical reaction of interest may be ascertained to be K-adiabatic or K-active, e.g., by following its time evolution using classical trajectories[18] in a unimolecular or a bimolecular study. When a K's value is approximately constant as a function of time, such as been discerned for ozone,[15,18] then such may be an indication of K exhibiting adiabaticity and may minimally be sharing energy with the remaining degrees of freedom, such as with vibration.

The utilization of an appropriate Eckart frame[61] embedding for investigating K, rather than a simpler instantaneous inertial tensor axes body fixed frame, may be useful to minimize the Coriolis coupling between the rotation and vibration, so in turn to minimize any artifact in causing unwanted undulation in the value of K upon its investigation and reporting.

A rotation and vibrationally excited molecule may possess a sufficient amount of energy to dissociate; however, it may do so only if its K is less than a K_{max} given by[19,20] $K_{max} = [2(E - E_{diss}) - J^2/\sqrt{\langle I_2 \rangle \langle I_3 \rangle}]/[1/\langle I_1 \rangle - 1/\sqrt{\langle I_2 \rangle \langle I_3 \rangle}]^{1/2}$ where $E_{diss} = E - E_{rot}$, $\langle I_i \rangle$ are the averaged principle moments of inertias and K may take up values ranging from $-J$ to J. In the Eckart frame,[61] the K_{max} may be appropriately adapted. For such values of K that satisfy $|K| > K_{max}$, then the vibrational energy, in particular, for a relevant reaction coordinate, is less than

the dissociation barrier and the excited molecule would not be able to dissociate. This has been observed for the ozone molecule for a unimolecular process[19,20] and can be investigated for a bimolecular process for ozone and in other systems.

B. Analytic comparison of the *K*-active and *K*-adiabatic populations of reactive complexes

In RRKM theory, an inequality between the K-active and the K-adiabatic systems has been discussed for a fixed TS[21] and found valid independent of whether or not the position of the TS depends on K and/or J (variational form of RRKM theory) and whether a 1-TS or a 2-TS expression is used for k_{rec} (adiabatic).[15] Likewise, herein, we proceed to inquire on how the K-adiabatic and K-active rates for a physical system described by master equations, Eqs. (13) and (14), compare to each other and elucidate the inequalities, when RRKM theory is used to determine the k_r and k_d in the populations. We first proceed to compare the K-active and K-adiabatic populations with each other in this section. This comparison informs on the physical circumstances on when the K-active population is expected to be greater or equal to the K-adiabatic population, which in turn yields further insight into the inequality of recombination rates for the energy regimes.

It is observed from Eqs. (29) and (33) that the K-adiabatic and K-active populations, each depends on the quantities k_r, k_d, and the Z_{LJ}, for the energy region $E > E^*$ and so they are used in the analysis which then leads to an emergence of specific conditions, on the inequalities of the K-active population of the reactive complexes $g(EJ)$ to the K-adiabatic $\sum_K g(EJK)$ population for an arbitrary intermolecular energy transfer model for a single well. An analysis is subsequently made for the $E \leq E^*$ region. In Ref. 62, the rationale for the selection of the test conditions is discussed. For the $E > E^*$ region (a) if $k_r(EJ)/\sum_K k_r(EJK)$ > $k_d(EJ)/\sum_K k_d(EJK)$ then $g(EJ)_+ > \sum_K g(EJK)_+$[62] or (b) if $k_r(EJ)/\sum_K k_r(EJK) = k_d(EJ)/\sum_K k_d(EJK)$, then $g(EJ)_+$ = $\sum_K g(EJK)_+$.[62] Upon noting the definitions of k_r and k_d, the test condition for case (b) implies that $1 = N^*(EJ)$ $/ \sum_K N^*(EJK) = [N^*(EJ)/\sum_K N^*(EJK)][\sum_K \rho(EJK)/\rho(EJ)]$, upon necessarily assuming that $\sum_K \rho(EJK)/\rho(EJ) = 1$ and $N^*(EJ)/\sum_K N^*(EJK) = 1$. This physical situation would only arise when the criterion $N^*(EJ)/\sum_K N^*(EJK) = 1$, and so case (b) is less probable than case (a), e.g., for ozone at TS.[15] Finally, the case $k_r(EJ)/\sum_K k_r(EJK) < k_d(EJ)/\sum_K k_d(EJK)$ does not arise physically, since the latter inequality implies $1 \leq N^*(EJ)/\sum_K N^*(EJK) < [N^*(EJ)/\sum_K N^*(EJK)][\sum_K \rho(EJK)/\rho(EJ)]$, but the last inequality is violated, upon also noting that $\sum_K \rho(EJK)/\rho(EJK) \leq 1$. A qualitative physical picture of the test condition (a) states that if the rate of association for K-active relative to its K-adiabatic counterpart is greater relative to the ratio of dissociations

then, expectedly the K-active populations accumulate more so relative to the K-adiabatic case. Upon extending this logic to case (b), then the K-active and K-adiabatic populations are equal because the rate of association for K-active to K-adiabatic is the same as dissociation rate for K-active to K-adiabatic.

The relation $k_r(EJ) \geq \sum_K k_r(EJK)$ is expected, since $N^*(EJ) \geq \sum_K N^*(EJK)$, upon noting the definition of k_r, where a proof is given in Ref. 15. As an example, for the formation of the metastable ozone molecule, values of $K \leq 5$ make the greatest contribution to the number of states at the transition state, for a typical $J \approx 15$,[15] where $N^*(EJ) > \sum_K N^*(EJK)$ for ozone, and $k_r(EJ)$ based on RRKM theory was found to be greater than $k_r(EJK)$, and the same inequality held between the comparison of the averaged thermal rates, a factor of 2, between the temperatures, 130 and 373 K.[15]

For the $E \leq E^*$ region, from Eq. (30) for $g(EJK)_-$, we have for the K-adiabatic population distribution function, $g_{eq}(E = 0, JK) = \rho(E = 0, JK)/Q$, and its K-active analogue is $g_{eq}(E = 0, J) = \rho(E = 0, J)/Q$. In a physical scenario, whereupon K is adiabatic and its value in phase space is restricted to a tighter interval relative to an active K, then $\rho(EJ) \geq \sum_K \rho(EJK)$, where the inequality may arise since $\rho(EJK) = 0$ for certain select K's, in contrast to an active K, so to lower the K-adiabatic density of states. Thus, $g(EJ)_- \geq \sum_K g(EJK)_-$ is expected at all pressures, for a given temperature, where Q is the same partition function for both the K-active and K-adiabatic cases. For example, a study on the evolution of K as a function of time in a unimolecular classical trajectory sampling of $O_3 + Ar$ reported results on a pseudo-adiabatic behaviour of K, e.g., $K \sim 11$, for a time duration up to 100 ps, for O_3 near the dissociation energy, so to restrict the K-adiabatic density of states for the metastable O_3.[18] However, as pressure increases, the collision of complexes with the bath gas may facilitate K to sample a larger range of interval and effectively may give rise to $g(EJ)_- \cong \sum_K g(EJK)_-$.

Additional physical considerations, for both energy regions, include how the K-motion evolves in the intermediate complex as a function of time, the efficacy of energy transfer with the bath gas as a function of pressure, and its impact on the modulation of K. Subtleties abound whereby when the initial K is small, e.g., $K \cong 1$, from a bimolecular formation, and thereafter energy may flow from the vibrational degrees of freedom so may serve to "heat" the K rotational degree of freedom, when the intramolecular energy transfer is effective, and then broaden the range of K as a function of time.[18] The time between collisions, τ, and the efficacy of the intramolecular energy transfer between rotation and vibration play an important role, whereby as τ increases then smaller K's may reach a higher value, unless if rotation and vibration reach internal equilibrium faster than τ, where then no dependence of intramolecular energy transfer on τ would be expected.[18] A discussion related to these matters, concerning the recombination rate, is expounded in Sec. V C.

C. Analytic comparison of the *K*-active and *K*-adiabatic forms of the master equations for the recombination rate constants at limiting pressures

1. High pressure limit

At the high pressure limit, $Z_{LJ} \to \infty$, for the energy region $E > E^*$, the first and second terms in the right hand side of the *K*-adiabatic master equation, Eq. (13), cancel each other, and so the right hand side of Eq. (13) remains with its third term where upon its reduction, after substituting for $g(EJK)_+$ there from Eq. (29), yields the expression $k_{rec}(EJK) = (hQ)^{-1}N^*(EJK)e^{-E/kT}$. The details of the proof are given in Appendix G. A similar analysis for the high pressure limit expression for the *K*-active master equation yields $k_{rec}(EJ) = (hQ)^{-1}N^*(EJ)e^{-E/kT}$. So, the *K*-adiabatic and *K*-active master equations at the high pressure limit each reduce, respectively, to the well known RRKM theory high pressure limit expression[16,63] for the *K*-active and its *K*-adiabatic counterpart, for the recombination rate constant.

At the high pressure limit, but for the energy region $E \le E^*$, we again have the first and second terms in the *K*-adiabatic master equation, Eq. (13), cancel each other, and the third term is also zero since $k_d(EJK) = 0$ appearing there, so $k_{rec}(EJK) = 0$, for this energy region (proof given in Appendix G). Similarly, we have for the *K*-active case $k_{rec}(EJ) = 0$. Thus, at the high pressure limit, the contributions to the recombination rate constant arise only from the energy region $E > E^*$, for both the *K*-adiabatic and *K*-active cases.

An analytic comparison between the *K*-active and *K*-adiabatic k_{rec}'s, at the high pressure limit, then yields $k_{rec}(EJ) > \sum_K k_{rec}(EJK)$ since $N^*(EJ) > \sum_K N^*(EJK)$ at the TS, and $k_{rec}(EJ) = \sum_K k_{rec}(EJK)$ when $N^*(EJ) = \sum_K N^*(EJK)$ at its TS.[15]

One may inquire on the expectations for the degree of agreement for *K*-active and *K*-adiabatic recombination rate constants from a master equation at the high pressure limit. We draw upon previous investigations based on classical trajectory[18] and our calculation from RRKM theory for ozone formation at the high pressure limit to form insight and initiate expectations on this matter. Since the high pressure form of the master equation reduces to the high pressure form of RRKM theory at the high pressure limit, as noted in the beginning of this section, then an RRKM theory calculation may be calculated for this pressure regime, for comparing the *K*-active and *K*-adiabatic recombination rate constants. The high pressure limit form of RRKM theory yields ~0.9 for the ratio of the *K*-adiabatic to the *K*-active recombination rate constant for ozone formation at 300 K, using an "any-looseness" model[64] of the ozone complex at the transition state, which takes into account the natural tightness of the complex at the TS, and quantum counting for $N^*(EJ)$ and $N^*(EJK)$ upon using a ground state potential energy surface[65] for ozone in the calculations. The remaining small discrepancy reflected in the ratio arises from the enhanced knowledge of the *K* dependence of the passage function at the TS, $N^*(EJK)$, as the flux traverses the transition state, compared to the calculation in the *K*-active case. Omitting

the allowed *K*'s in a *K*-active calculation, or to either let *K* exceed the bound of $-J$ to J, by approximating with a free exchange of energy between vibrational modes and the *K* term, or to only consider *J* and assume *K* is averaged within the *J* limits without delineating the allowed *K*'s at the transition state, would yield a discrepancy of about a factor of 2 or greater when compared to the *K*-adiabatic rate. At the high pressure limit, the agreement between the *K*-active and *K*-adiabatic recombination rate constants for ozone is close to unity, and perhaps in other reactions, the physics may permit a variance about a factor of 2 and can be further investigated for various systems. The final ratio may not be unity in some circumstances for specific systems, because of possible unique geometric constraints, e.g., the shape of the molecule may render forth directional effects to become important at the transition state when considering the principle axis associated with *K*, interacting with the bath gas, to impede the formation of a metastable complex for selected *K*'s, and such a possible *K* dependence of complex formation can be further investigated, and the omission of this information in a *K*-active calculation may give rise to a discrepancy. The Chaperon mechanism (i.e., bath gas interactions with O and O_2) for assisting the formation of ozone has been discussed in the literature.[66,67] Intramolecular and intermolecular energy transfers, as a function of pressure, also play a role in facilitating *K* to explore its range discussed next, whereby the noting of their physics is then extended to analyze the high pressure limit.

A previous trajectory based study[18] on the intramolecular and intermolecular energy transfer for ozone showed that the excited ozone molecules are "cooled" in collisions with argon atoms with a mechanism that involves both intramolecular and intermolecular energy transfers, where the rotation-translation channel for energy transfer plays a dominant role relative to a vibration-translation channel.[18] In successive collisions with argon, the *J* and the *K* gradually relaxed to their average equilibrium values, $J_{eq} \approx 17$ and $K \approx 3.5$ (classical value reported[18]) for collision energies $E_{coll} = 200$ cm^{-1}.[18] Angular momentum $J \approx 15$ and *K* up to ~5 are the values that contribute the most to the recombination rate constant for ozone formation.[15] It has been found from classical trajectories[18] that the time between collisions, τ, controls the energy loss per collision for the internal energy E_{int}, the vibrational energy E_v, and by $E_{int} = E_v + E_r$, the rotational energy E_r of the ozone molecule. The equilibrium rotational energy of ozone, with multiple collisions (precise number of collisions unspecified in Ref. 18) with argon atoms, decreased from 233 cm^{-1} to 203 cm^{-1}, as τ decreased from 170 ps to 6 ps, reported[18] to be caused by a smaller amount of intramolecular energy transfer from vibration to rotation as the time between collision decreased. As such, the mean of the magnitude of *K* would be expected to reach a lower value, as the magnitude of *J* would be smaller for a lowered rotational energy. The total internal energy of ozone appeared to be greater by at least ~600 cm^{-1} as τ decreased from 170 to 6 ps, by the 100th collision (results noted in Figure 7 of Ref. 18, whereby a subtlety may be noted that the 6 ps and the 170 ps trajectory based data reported an initial total internal energy of 0 and 200 cm^{-1}, respectively, relative to the dissociation energy of

ozone, prior to any collision).[18] The J dependence of the total internal energy transfer, ΔE_{int}, is commonly explained in terms of the Landau-Teller model[68] and based on the comparison of characteristic time scales of collision, rotation, and vibration.

In the high pressure limit, as $Z_{LJ} \to \infty$, the time between collisions has $\tau \to 0$, and so one may posit, upon extending the physical premise at the lower pressures, that the multiple collisions interacting with the rotational mode would exchange energy, but now more rapidly, and facilitate K to reach an equilibrium value. Meanwhile, the Coriolis coupling (constant ~ 0.5 cm^{-1},[69] for coupling the symmetric and antisymmetric stretching vibrations of ozone) is of course ever present and is the driving force of $K(t)$,[19] and the constrained energy sharing with the K degree of freedom would continue to take place on its own time scale (greater than the characteristic time scale, 60 fs, of the principle moment of inertias of O$_3$),[19] where the value of K for ozone has been observed to be pseudo-adiabatic for times up to 500 ps according to our study of trajectories. Upon extending the premise of the logic of the collision time and energy transfer at the lower pressures to the high pressure limit, then the multiple collisions play a dominant role in cooling and heating the rotational degree of freedom until an equilibrium value is reached. The vibrational channel may also participate to a greater degree in exchanging energy with the bath gas, than is found at the lower pressures,[18] and would again serve to contribute in settling K to an equilibrium value, after multiple collisions at the high pressure, and may be a point of investigation in the future.

In finalizing the above notings and analysis, the K-adiabatic recombination rate constants for ozone approaching the value of the K-active rate, at the high pressure limit, ratio of about 0.9, may be noted to be consistent with the aforementioned analysis, and whereby the multiple collisions interacting with the rotational channel may facilitate and assist the K to explore a wider range beyond its adiabatic values in its J limit, even upon noting the physical back-drop in which the intramolecular energy transfer is restricted in the ozone molecule as observed from trajectory studies. The collisions with the bath gas molecules would in turn supply a physical channel for K to explore its possible range, and circumvent an intramolecular energy restriction on the modulation of the value of K. Generally, in turn, in a numerical treatment of a thermal k_{rec} for a given reaction, the coverage of K is to be noted when determining $\sum_{JK} N^*(EJK)$ and $\sum_{JK} \rho(EJK)$.

Finally, some subtleties regarding $N^*(EJK)$ are delineated. In a calculation of $N^*(EJK)$ from variational RRKM theory,[16,17] and then using it in a master equation, or in an RRKM theory calculation, it is beneficial to study $N(EJK)$ vs R, extending to large R's, center-to-center distance of reaction coordinate, up to 10 bohrs radius when considering ozone, or possibly a greater distance for other reactions. For example, it is found that although $N^*(EJK)$ for ozone may be nonzero for select values of (EJK), e.g., for $E = 0.2 \, kT$ above the dissociation limit, $J = 20$ and $K = 5$ at the transition state, $R = 5.2$ bohrs radius, however, at larger distances of $R \geq 8.3$ bohrs, $N(EJK) = 0$, and so the incoming flux would have been obstructed at the larger distance, and not reach the transition state, and so in the absence of this noting, the flux and, hence, the recombination rate constant would have

been overestimated. This highlights the relationship between geometry, total energy, and angular momentum of the complex on when it to be physically reified and indicates that noting the history of the flux upon reaching the transition state is also important on delineating to include or exclude a given J and K value in phase space, for contributing to $N^*(EJK)$ and hence to $g(EJK)$ and to the recombination rate constant at a given pressure and temperature. A K-active calculation omitting these subtleties would contribute to discrepancies with a K-adiabatic calculation, and such errors can be avoided, when determining the bimolecular recombination rates for reactions of interest.

2. Low pressure limit

At the low pressure limit, i.e., as $Z_{LJ} \to 0$, for the energy region $E > E^*$, upon comparing[70] the K-adiabatic and K-active based master equations, Eqs. (13) and (14), respectively, yields $k_{rec}(EJ) > \sum_K k_{rec}(EJK)$ when $N^*(EJ) > \sum_K N^*(EJK)$ at the TS, or $k_{rec}(EJ) = \sum_K k_{rec}(EJK)$ when $N^*(EJ) = \sum_K N^*(EJK)$ at its TS. These results on the comparison of the relative magnitude of the K-adiabatic and K-active k_{rec}'s agree with that found in an earlier work[15] on the k_{rec}'s, at low pressure, derived from RRKM theory.

For the energy region $E \leq E^*$, as $Z_{LJ} \to 0$, there is no contribution to either K-active or K-adiabatic recombination rate constant, since each term, in Eqs. (13) and (14), is zero.

In the low pressure limit, as $Z_{LJ} \to 0$, since collisions with the intermediate complex are absent, then it is the intramolecular energy transfer process that influences the modulation of the value of K via the Coriolis coupling, and as the sole driving force of K, rendering it K-active or K-adiabatic. Thus, at the low pressure limit, the discrepancy between the K-active and K-adiabatic rates may indeed be larger than at the high pressure limit, since the increase of τ brings forth the issue of intramolecular energy transfer and its dampening effect on the modulation of K to the forefront of the analysis[19] and serves to restrict the range of K in ozone, or in other systems when the intramolecular energy coupled to the K degree of freedom is constrained.

A previous calculation of the K-active to K-adiabatic recombination rates based on RRKM theory that included a single exponential model for intermolecular energy transfer, at low pressure (1 atm, 100 ps between collisions), yielded a ratio of 2.1 at $T = 298$ K, prior to corrections for recrossings (20%) and quasi-periodicity (11%), and after the latter corrections the ratio became 1.7.[15] A detailed calculation of the master equations at the low pressure limit and for a varying pressure would provide a requisite accurate comparison and can be fruitful, and as such is planned to partake for the ozone recombination. The investigation of other reactions would provide insight and be beneficial, e.g., Cl + C$_2$H$_2$ → C$_2$H$_2$Cl.[21] In the acetylene reaction, a sensitivity of the pressure and temperature dependent association rate constant using RRKM theory has been noted and challenges on agreement with experiment were described in Ref. 21.

D. Treatment of population and master equations

Under the condition that the steady state condition, $dg(EJK)/dt = 0$, holds in a bimolecular reaction of interest, such as after a short initial period where K-adiabatic populations $g(EJK)$ relax toward a steady state,[41] then the closed form analytic solutions, i.e., the populations, reported in Section III, may be used to determine the bimolecular recombination rate constant as a function of temperature.[27,71] The aforementioned analysis also applies when K is active. For an investigation of a time-dependent population, the expressions for the recurrence relations may be amenable.

For calculating the steady-state populations, e.g., from Eq. (32), the $N^*(EJK)$ and $\rho(EJK)$ can be determined separately on the side, and similarly for the K-active $N^*(EJ)$ and $\rho(EJ)$[72,73] (e.g., using a Beyer-Swinehart algorithm)[74] and then each function quarried for k_d in the integral of the second term of Eq. (32).

For the usual treatment of the master equations, the incorporation of the K-adiabatic resolved states in the eigenvalue method or in the stochastic based method master equations can be useful when the K-adiabatic regime is physically relevant. Each aforementioned method can proceed to surmount its own challenge regarding the matter. The incorporation of the K-adiabatic resolved states in the eigenvalue method may increase the size of the matrix to be diagonalized and associated challenges on efficiency may be explored and circumscribed. For a stochastic approach, upon the incorporation of the K resolved states in the method, one may explore the efficiency for convergence of rates and investigate the normalization of the collision step size distribution when the density of states is sparse,[75] for a resolved E, J, and K. A successful incorporation of J and K states into either methods may be useful for determining the bimolecular rate constants for reactions of interest.

VI. SUMMARY AND CONCLUDING REMARKS

A K-adiabatic based master equation has been derived for the bimolecular recombination rate constant, considered for both single and multiple well chemical reactions. Exact analytic solutions, the K-adiabatic and K-active steady-state populations of reactive complexes, were derived in closed form for the master equations using theory of integrals (with Fredholm theory). The solutions are for an arbitrary intermolecular transfer energy model, illustrated for a single exponential case and may also accommodate others, e.g., double exponential, Gaussian, step-ladder, and near-singularity models. The recurrence relations were also given for evolving the populations as a function of time, and for treating the energy dependence of the populations for the time independent case.

An analytic comparison was made for the relative magnitude of the K-active and K-adiabatic populations, where the latter is less than or equal to the former. Analytic comparison of the K-active and K-adiabatic based bimolecular master equations was also made for the recombination rate constants, $k_{rec}(K$-active$)$ and $k_{rec}(K$-adiabatic$)$, at the low and high pressure limits. At the high pressure limit, the k_{rec} for

each K-adiabatic and K-active master equation was shown to be equivalent, respectively, to the K-adiabatic and K-active forms of RRKM theory expressions at the high pressure limit, whereby only the energy region $E > E^*$ contributed to the recombination rate constant. This equivalence at the high pressure limit may serve as a check on the calculation of rates based on master equations, for reactions of interest. The O_3 and its recombination exhibit an adiabatic K, although, the calculated ratio of the K-adiabatic to the K-active recombination rate of O_3 at the high pressure limit yielded about 0.9, and the reasons for it as related to the intermolecular energy transfer were discussed, and expectations on the matter delineated. The pressure and temperature dependence of the K-adiabatic and K-active populations of ozone and its rate of formation using master equations will be investigated elsewhere.

APPENDIX A: INTERMOLECULAR ENERGY TRANSFER MODELS FOR $Z(E, E')$

For a double exponential model of energy transfer between a molecule and its bath gas, we have[1]

$$Z(E,E') = Z_o[\exp(-|E - E'|/\gamma) + c\exp(-|E - E'|/d)],$$
$$E' < E, \tag{A1}$$
$$Z(E,E') = Z_o[\exp(-|E - E'|/\gamma') + c\exp(-|E - E'|/d')],$$
$$E' > E, \tag{A2}$$

where Z_o is a constant and γ, γ' and d, d' are related by detailed balance. The γ and γ' are the same as those of the single exponential model and the constants c and d may be obtained from a classical trajectory calculations data for vibrational energy transfer.

For a Gaussian model of intermolecular energy transfer,[1,35,36]

$$Z(E,E') = \begin{cases} Z_o e^{-(E-E')^2/\gamma^2}, & E' < E \\ Z_o e^{-(E'-E)^2/\gamma'^2}, & E' > E \end{cases} \tag{A3}$$

for use in the K-adiabatic master equation, Eq. (17), where γ and γ' are the deactivation and activation constants, in which they are related to each other by detailed balance. The Z_o contains a normalization constant multiplied by the Lennard-Jones frequency.

For a step-ladder model for intermolecular energy transfer,[37–39] we have

$$Z(E,E') = Z_o\sigma, \tag{A4}$$

where σ is a constant when $|E - E'| = \langle \Delta E \rangle_{E_d}$; otherwise $Z(E, E') = 0$, and the "up" transitions would be given by detailed balance,[37–39,76] which can be utilized in the master equation, Eq. (13). A complex step-ladder model with a distribution of step may also be considered.[37]

Typically, the "up" transitions have been neglected in using the step-ladder model according to an assumption that high level of excitations is present in a chemically activating system, and collisions may make it less likely to populate higher energy levels.[52] As the neglect of the "up" transition may violate detailed balance, then a step size sufficiently relatively large compared to kT has been used so that $\exp(-\Delta E/kT) \sim 0$,[52] and as such one may carefully examine for a given physical situation, especially when $\Delta E \leq kT$.

For a near-singularity model, about a neighborhood of $E - E' = 0$, the $Z(E, E')$ for the intermolecular energy transfer is given by[27]

$$Z(E, E') = \begin{cases} Z_o[1 + \beta(E - E')^{-\alpha}]e^{-(E-E')/\gamma}, & E' < E \\ Z_o[1 + \beta(E' - E)^{-\alpha}]e^{-(E'-E)/\gamma'}, & E' > E \end{cases},$$
(A5)

where γ and γ' are the same as those of the single exponential model, and α and β are parameters obtained, e.g., from classical trajectory data.

APPENDIX B: RECURRENCE RELATIONS FOR THE STEADY-STATE MASTER EQUATION

The following method, based on discretization, provides the recurrence relations for finding the energy dependence of the steady-state population of the integral master equation, Eq. (13). In the K-adiabatic master equation in the form of Fredholm equation, Eq. (17), the integral $\sum_{J'K'} \int Z(E, E')g(E'J'K')dE'$ can be replaced by a finite sum according to one of the approximate formulae of quadrature. For example, for simplicity of an illustration, according to the rectangle formula[45]

$$\sum_{J'K'} \int_a^b Z(E, E')g(E'J'K') \approx h \sum_{k=1}^n \sum_{J'K'} Z(E, E_k)g(E_k J'K'),$$
(B1)

where $h = (b - a)/n$ and $E_k = a + kh$. Substituting Eq. (B1) into the K-adiabatic master equation, Eq. (17), gives

$$g(EJK) = \lambda h \sum_{k=1}^n \sum_{J'K'} Z(E, E_k)g(E_k J'K') + f(EJK).$$
(B2)

Let us replace E_k in Eq. (B2) by $E_1, E_2, \dots, E_n$. We then obtain a system of linear algebraic equations for $g(E_1 JK) \dots g(E_n JK)$,

$$g(E_i JK) = \lambda h \sum_{k=1}^n \sum_{J'K'} Z(E_i, E_k)g(E_k J'K') + f(E_i JK),$$
(B3)

with $i = 1, 2, \dots n$. Solving Eq. (B3), we find the approximate values of $g(EJK)$ at the points $E_1, E_2, \dots, E_n$. The use of any interpolation formula[45] then yields an approximate expression for $g(EJK)$ in the whole interval. Instead of the rectangle formula, one may of course choose other integration schemes,

such as the trapezoidal rule, Simpson's rule, or others, for attaining optimal accuracy.[45] The K-active counterpart of Eq. (B3) is then given by

$$g(E_i J) = \lambda h \sum_{k=1}^n \sum_{J'} Z(E_i, E_k)g(E_k J') + f(E_i J),$$
(B4)

where the K-degree of freedom has been assumed averaged over at the outset.

APPENDIX C: PROOF FOR $g(EJK)$, $g(EJK)_+$, $g(EJK)_-$, EQS. (20), (24), AND (25), AS SOLUTIONS OF THE MASTER EQUATION, EQ. (17), AND DERIVATION FOR $\hat{A}$, EQ. (21)

We first proceed to prove, by substitution, that $g(EJK)$, Eq. (20), is a solution of the K-adiabatic master equation, Eq. (17), and derive the coefficient $\hat{A}$, Eq. (21), in $g(EJK)$. We consider the K-adiabatic master equation, Eq. (17), in the form of Fredholm integral equation, and substitute $g(EJK)$, Eq. (20), into the left hand side of Eq. (17), and also in its right hand side, inside the integral sign, to yield

$$f(EJK) + \lambda \hat{A} - \lambda \sum_{J'K'} \int_{E_O}^{\infty} Z(E, E')[f(E'J'K') + \lambda \hat{A}]dE'$$

$$= f(EJK).$$
(C1)

Canceling $f(EJK)$ from the right and left hand sides of Eq. (C1) and distributing the terms inside the integral sign then yield

$$\lambda \hat{A} - \lambda \sum_{J'K'} \int_{E_O}^{\infty} Z(E, E')f(E'J'K')dE'$$

$$- \lambda^2 \hat{A} \int_{E_O}^{\infty} Z(E, E')dE' = 0,$$
(C2)

where a sum over J' and K' has been performed in the third term of the left hand side of Eq. (C2). In Eq. (C2), the $\hat{A}$ appears outside of the third integral, since $\hat{A}$ is independent of E'. Upon readily eliminating λ in Eq. (C2) and factoring $\hat{A}$ then yield

$$\hat{A}\left[1 - \lambda \int_{E_O}^{\infty} Z(E, E')dE'\right] = \sum_{J'K'} \int_{E_O}^{\infty} Z(E, E')f(E'J'K')dE'.$$
(C3)

Solving for $\hat{A}$ in Eq. (C3) then yields

$$\hat{A} = \frac{\sum_{J'K'} \int_{E_O}^{\infty} Z(E, E')f(E'J'K')dE'}{1 - \lambda \int_{E_O}^{\infty} Z(E, E')dE'}.$$
(C4)

The numerator in Eq. (C4) is the f_1 defined in Eq. (22), while $[\int_{E_O}^{\infty} Z(E, E')dE']^{-1}$ is λ_1 defined in Eq. (23), where both substitutions into Eq. (C4) then yield Eq. (21), $\hat{A} = \frac{f_1}{[1-\lambda/\lambda_1]}$. Thus, $g(EJK)$ is a solution to the master equation with its

coefficient $\hat{A}$. A similar analysis may be used in proving that $g(EJ)$ is a solution for its K-active master equation.

We next prove, by substitution, that $g(EJK)_+$, Eq. (24), for the energy region, $E > E^*(JK)$, is a solution of the K-adiabatic master equation, Eq. (17). Upon inserting $g(EJK)_+$, Eq. (24), into the K-adiabatic master equation, Eq. (17), yields

$$f(EJK) + \frac{\lambda\lambda_1 f_1}{\lambda_1 - \lambda} - \lambda \sum_{J'K'} \int_{E_o}^\infty Z(E',E)\left[f(E'J'K') \right.$$
$$\left. + \frac{\lambda\lambda_1 f_1}{\lambda_1 - \lambda} \right] dE' = f(EJK). \tag{C5}$$

Upon canceling $f(EJK)$ from both sides of Eq. (C5), distributing the $Z(E',E)$ under the integral sign, and factoring out a λ term and eliminating it yield

$$\frac{\lambda_1 f_1}{\lambda_1 - \lambda} - \sum_{J'K'} \int_{E_o}^\infty Z(E',E) f(E'J'K') dE'$$
$$+ \frac{\lambda\lambda_1 f_1}{\lambda_1 - \lambda} \int_{E_o}^\infty Z(E',E) dE' = 0, \tag{C6}$$

where a sum over J' and K' has been performed in the third term. Noting that the second term in Eq. (C6) is f_1, defined in Eq. (22), and then factoring the f_1 and eliminating it from Eq. (C6) then yield

$$\frac{\lambda_1}{\lambda_1 - \lambda} - 1 - \frac{\lambda_1}{\lambda_1 - \lambda} \int_{E_o}^\infty Z(E',E) dE' = 0. \tag{C7}$$

Also, upon noting that $\lambda_1 = [\int_{E_o}^\infty Z(E',E)dE']^{-1}$ from Eq. (23), then λ_1 and $\int_{E_o}^\infty Z(E',E)dE'$ cancel in the third term on the left hand side of Eq. (C7), to yield

$$\frac{\lambda_1}{\lambda_1 - \lambda} - 1 - \frac{\lambda}{\lambda_1 - \lambda} = 0. \tag{C8}$$

Upon rearranging the terms in Eq. (C8) then yields $\lambda_1 - \lambda = \lambda_1 - \lambda$, which then completes the proof. An analogous analysis may prove that the K-active $g(EJ)_+$ is a solution of its master equation.

We next prove that for the energy region $E \le E^*(JK), g(EJK)_-$, Eq. (25), is a solution of its K-adiabatic master equation, Eq. (17). Upon inserting $g(EJK)_- = \lambda_1\hat{C}$, Eq. (25), into the K-adiabatic master equation, Eq. (17), onto its left hand side and the right hand side inside the integral sign, yields

$$\lambda_1\hat{C} - \lambda \sum_{J'K'} \int_{E_0}^\infty Z(E',E)\lambda_1\hat{C} dE' = 0. \tag{C9}$$

Since $E \le E^*(JK)$, the $f(EJK)$ that would have appeared on the right hand side of the master equation is set to zero in Eq. (C9), as the recombination and dissociation rate constants in the $f(EJK)$ are each zero below the critical energy limit. Since $\lambda_1\hat{C}$ does not depend on E', it may be factored outside of the integral sign in the second term of Eq. (C9). The

constant $\hat{C}$ may then be eliminated in Eq. (C9). Also noting that $\lambda_1 = \lambda$ for $E \le E^*(JK)$, since $k_d(EJK) = 0$ in λ, and also that $\lambda_1 = [\int_{E_o}^\infty Z(E',E)dE']^{-1}$ from Eq. (23), then λ_1 and $\int_{E_o}^\infty Z(E',E)dE'$ cancel in Eq. (C9), which then finally yield Eq. (C9) to be $\lambda_1 = \lambda_1$, which completes the proof. An analogous analysis may prove that the K-active $g(EJ)_-$ is a solution of its master equation.

APPENDIX D: BOUNDARY CONDITIONS FOR g_+ AND g_- AND ANALYTIC CONTINUATION

Herein, we proceed to elucidate the boundary conditions whereupon $g(EJK)_+ = g(EJK)_-$ for the K-adiabatic case, by using complex analysis to check for singularity and convergence of each function for each energy domain $E > E^*(JK)$ and $E \le E^*(JK)$, and analytic continuation across the boundary.[77,78] A similar analysis may be applied to a K-active case. We first consider $g(EJK)_+$ for the energy region $E > E^*(JK)$. Upon applying a Fourier transform, $f(z) = \int_{-\infty}^\infty e^{2\pi i z E} f(E)dE$, to $g(EJK)_+$, we obtain $|g(zJK)_+|$

$= \left| \int_{-\infty}^\infty e^{2\pi i z} g(EJK)_+ dE \right| = \left| \int_{E^*}^\infty e^{2\pi i z} g(EJK)_+ dE \right|$, where the justification for the last equality rests upon $g(EJK)_+ = 0$ for $E \le E^*(JK)$. Upon letting $z = u + iv$, then $|g(zJK)_+|$

$= \left| \int_{E^*}^\infty e^{2\pi i u E} e^{-2\pi v E} g(EJK)_+ dE \right| \le \left| \int_{E^*}^\infty e^{-2\pi v E} g(EJK)_+ dE \right|$. If a solution exists for $g(zJK)_+$ such that $|g(EJK)_+| < x_1 e^{2\pi v' E}$ as $E \to \infty$ where $v' < 0$, so $|g(EJK)_+| \to 0$ as $E \to \infty$, then we have

$$|g(zJK)_+| < \int_{E^*}^\infty e^{-2\pi v E} x_1 e^{2\pi v' E} dE = \frac{-x_1 e^{2\pi(v'-v)}}{2\pi(v' - v)}. \tag{D1}$$

Thereby, in the part of the upper half plane where $\text{Im } z = v > v', |g(zJK)_+|$ has no singularity. So, $g(zJK)_+$ is an analytic function in the half plane of the z-plane for which $\text{Im } z > v'$.

Now upon considering $g(EJK)_-$, we Fourier transform $|g(zJK)_-| = \left| \int_{-\infty}^\infty e^{2\pi i z E} g(EJK)_- dE \right|$. Again letting $z = u + iv$, we have $|g(zJK)_-| = \left| \int_{-\infty}^{E^*} e^{2\pi i u E} e^{-2\pi v E} g(EJK)_- dE \right|$

$\le \int_{-\infty}^{E^*} e^{-2\pi v E} |g(EJK)_-| dE$. We seek a solution such that $|g(zJK)_-| < x_2 e^{2\pi v'' E}$ as $E \to -\infty$ where $v'' > 0$, and hence $g(EJK)_- \to 0$ as $E \to -\infty$, and thus we have

$$|g(zJK)_-| < \int_{-\infty}^{E^*} e^{-2\pi v E} x_2 e^{2\pi v'' E} dE = \frac{x_2}{2\pi(v'' - v)}. \tag{D2}$$

Thereby, in the part of the lower half plane where $\text{Im } z = v < v'', |g(zJK)_-|$ has no singularity. So $g(zJK)_-$ is an analytic function in the half of the z-plane for which $\text{Im } z < v''$. Since then $v' < 0 < v''$, and analytic continuation[77,78] is unique in this strip for select values of x_1, x_2, v, v', and v'' so $g(z)_- = g(z)_+$, then there exists an entire

function F in the complex plane that coincides in this region.

We now take the inverse transform of $|g(zJK)_+|$ and $|g(zJK)_-|$ of Eqs. (D1) and (D2), respectively, to yield

$$g(EJK)_+ = x_1 e^{2\pi E v'} |Ei[-2\pi(E - E^*)(v' - v)]|/2\pi,$$
$$E > E^*(JK), \ v' - v < 0 \qquad (D3)$$

and

$$g(EJK)_- = x_2 e^{2\pi E v''} |Ei[-2\pi(E - E^*)(v'' - v)]|/2\pi,$$
$$E \leq E^*(JK), \ v'' - v > 0. \qquad (D4)$$

The units of v, v', and v'' are inverse energy. The Ei denotes an exponential integral[45] in Eqs. (D3) and (D4), defined as $Ei(z) = \int_{-z}^{\infty} e^{-t}/t \, dt$, where the principal value of the integral is taken. The inverse transform was considered under the restriction of the conditions noted in Eqs. (D3) and (D4). At the boundary for a given (EJK), we have $g(EJK)_+ = g(EJK)_-$, upon using Eqs. (D3) and (D4), with the constants x_1 and x_2 selected to ensure the equality, and obeying the conditions $v' - v < 0$ and $v'' - v > 0$ for the two energy regions of E. Inserting $g(EJK)_+$ and $g(EJK)_-$ from Eqs. (D3) and (D4) into boundary condition Equation (27) then establishes the relationship between x_1, x_2, $f(EJK)$, λ, λ_1, and $\hat{A}$.

The aforementioned analysis also applies to the K-active boundary condition, whereby now the K degree of freedom has appropriately been averaged over at the outset and would be absent in each step of the above presentation.

APPENDIX E: A TRANSFORMATION OF SYSTEMS OF MASTER EQUATIONS TO A SINGLE EQUATION

In the steady-state approximation, when applicable, the system of integral master equations for a multiple chemical intermediates, in the absence of isomerization, for a bimolecular process is given by

$$g_i(EJK) - \lambda_i \sum_{j=1}^{n} \sum_{J'K'} \int_a^b Z_{ij}(E',E)g_k(E'J'K')dE' = f_i(EJK)$$
$$(E1)$$

with $i = 1, 2, \ldots, n$, for n given chemical intermediates. The a in the lower limit of integration may be assigned a minimum physics based value, while b, in the upper limit, may be selected such that convergence in g_i is achieved. Eq. (E1) is the counterpart of the single chemical intermediate master equation, Eq. (17), with the terms defined earlier following Eq. (17). The theory and the methods of solution, of systems of integral equations, Eq. (E1), are the same as for a single equation.

The system of integral equations, Eq. (E1), for which all Fredholm theorems[32] are satisfied, may be transformed into a single Fredholm integral equation of the second kind.[79] Let us introduce functions $\tilde{g}(EJK)$ and $\tilde{f}(EJK)$ on the interval $[a, nb - (n-1)a]$ by setting

$$\tilde{g}(EJK) = g_i(E - (i-1)(b-a), J, K), \qquad (E2)$$
$$\tilde{f}(EJK) = f_i(E - (i-1)(b-a), J, K), \qquad (E3)$$
$$\tilde{\lambda}(EJK) = \lambda_i(E - (i-1)(b-a), J, K) \qquad (E4)$$

for $(i-1)b - (i-2)a \leq E \leq ib - (i-1)a$. Let us define the kernel $\tilde{Z}(E',E)$ on the square $\{a \leq E \leq nb - (n-1)a, a \leq E' \leq nb - (n-1)a\}$ as follows:

$$\tilde{Z}(E,E') = Z_{ij}(E - (i-1)(b-a), E' - (j-1)(b-a)) \qquad (E5)$$

for $(i-1)b - (i-2)a \leq E \leq ib - (i-1)a$ and $(j-1)b - (j-2)a \leq E' \leq jb - (j-1)a$. Now system Equation (E1) can be rewritten as a single Fredholm equation,

$$\tilde{g}(EJK) - \tilde{\lambda}(EJK) \sum_{J'K'} \int_a^{nb-(n-1)a} \tilde{Z}(E',E)\tilde{g}(E'J'K')dE'$$
$$= \tilde{f}(EJK), \qquad (E6)$$

where $a \leq E \leq nb - (n-1)a$. If the kernels $Z_{ij}(E',E)$ are square integrable on the square $S = \{a \leq E \leq b, a \leq E' \leq b\}$ and the right hand sides $f_i(EJK)$ are square integrable on $[a,b]$, then the kernel $\tilde{Z}(E',E)$ is square integrable on the new square $S_n = \{a < x < nb - (n-1)a, a < t < nb - (n-1)a\}$, and the right hand side of Eq. (E6), $\tilde{f}(EJK)$, is square integrable on $[a, nb - (n-1)a]$. The solution $\tilde{g}(EJK)$ of Eq. (E6) may be partitioned into $\tilde{g}(EJK)_+$ for energy region $E > E^*(JK)$, and $\tilde{g}(EJK)_-$ when $E \leq E^*(JK)$.

Similarly, the K-active system of integral equations can take the form of a single integral master equation

$$\tilde{g}(EJ) - \tilde{\lambda}(EJ) \sum_{J'} \int_a^{nb-(n-1)a} \tilde{Z}(E',E)\tilde{g}(E'J')dE' = \tilde{f}(EJ),$$
$$(E7)$$

where the K degree of freedom was averaged over at the outset in the derivation.

APPENDIX F: ANALYTIC SOLUTIONS FOR SYSTEMS OF STEADY STATE K-ADIABATIC AND K-ACTIVE MASTER EQUATIONS

The possible and necessary conditions for the solution of the $g_i(EJK)$ for an i-th chemical intermediate, in the absence of isomerization, similarly follow that for a single intermediate $g(EJK)$, given earlier for Eqs. (24) and (25) for the energy regions, $E > E^*(JK)$ and $E \leq E^*(JK)$, respectively.

A solution of the steady-state K-adiabatic master equation, Eq. (E1), for the energy region $E > E^*(JK)$, for a multiple chemical intermediate, is given by

$$g_i(EJK)_+ = f_i(EJK) + \frac{\lambda_i \lambda_{1_i} f_{1_i}}{\lambda_{1_i} - \lambda_i}, \quad E > E^*(JK), \qquad (F1)$$

where $\lambda_i \neq \lambda_{1_i}$, and as a check, upon Eq. (F1)'s insertion into Eq. (E1) satisfies the master equation. The sub-index i in Eq. (F1) refers to the ith chemical intermediate, but otherwise similar in form to Eq. (24). In Eq. (F1), we have for its right hand side, $f_i(EJK) = \lambda_i k_{r_i}(EJK)A \circ BC$ and $\lambda_i = [\int_{E_o}^{\infty} Z_i(E,E')dE' + k_{d_i}(EJK)]^{-1}$, where the identifications

are also made for $f_{1_i} = \sum_{J'K'} \int_{E_o}^{\infty} Z_i(E,E') f_i(E'J'K') dE'$ and $\lambda_{1_i} = [\int_{E_o}^{\infty} Z_i(E,E') dE']^{-1}$.

For the energy region $E \le E^*(J)$, we have

$$g_i(EJK)_- = \lambda_{1_i} \hat{C}_i, \quad E \le E^*(JK), \qquad (F2)$$

where $\hat{C}_i = \frac{g_{eq_i}(0) c_E e^{-E/kT}}{\lambda_{1_i}}$ and g_{eq_i} is the i-th equilibrium population distribution for an i-th potential energy well. A similar analysis, with K averaged over, would yield results for the K-active counterparts of Eqs. (F1) and (F2).

APPENDIX G: PROOF FOR THE MASTER EQUATION REDUCING TO THE HIGH PRESSURE LIMIT FORM OF RRKM THEORY AT THE HIGH PRESSURE LIMIT

We provide a proof that at the high pressure limit, the master equation, Eq. (13), describing the K-adiabatic $k_{rec}(EJK)$, reduces to the high pressure limit form of RRKM theory,[16,63] and by extension a similar proof is valid for the K-active case where the K degree of freedom is averaged over. We first consider the energy region, $E > E^*(JK)$, and commence by demonstrating that the first two terms in Eq. (13) cancel at the high pressure limit, and in turn the third term is what remains and emerges as the high pressure limit of RRKM theory.

We solve Eq. (17) for $g(EJK)_+$,

$$g(EJK)_+ = \frac{\sum_{J'K'} \int_{E_o}^{\infty} Z(E',E) g(E'J'K')_+ dE'}{\int_{E_o}^{\infty} Z(E,E') dE' + k_d(EJK)} + \frac{k_r(EJK) A \circ BC}{\int_{E_o}^{\infty} Z(E,E') dE' + k_d(EJK)}, \qquad (G1)$$

where the definitions for $f(EJK)$, Eq. (18), and λ, Eq. (19), were used. We take the high pressure limit of Eq. (G1), as $Z_{LJ \to \infty}$, and apply L'Hopital's rule[80,81] (infinity-over-infinity case) to the first and second terms of Eq. (G1), and note again $Z_{LJ} = \int_{E_o}^{\infty} Z(E,E') dE'$ from the completeness requirement of the transition probability.[52–54] The application of L'Hopital's rule to Eq. (G1) yields

$$g(EJK)_+ = \sum_{J'K'} \int_{E_o}^{\infty} Z'(E',E) g(E'J'K')_+ dE', \qquad (G2)$$

where $Z(E',E) = Z_{LJ} Z'(E',E)$, and Eq. (G2) received all its contribution from the first term of Eq. (G1), since the application of the L'Hopital's rule to the second term in Eq. (G1) yields for the numerator, 0, and for its denominator, 1, with a result of $0/1 = 0$.[81] Upon inserting $g(EJK)_+$ from Eq. (G2) into the first term of the master equation, Eq. (13), yields a master equation

$$k_{rec}^+(EJK) A \circ BC = \sum_{J'K'} \int_{E_o}^{\infty} Z'(E',E) g(E'J'K')_+ dE' \times \int_{E_o}^{\infty} Z(E,E') dE' - \sum_{J'K'} \int_{E_o}^{\infty} Z(E',E) g(E'J'K')_+ dE' + k_d(EJK) g(EJK)_+, \qquad (G3)$$

where the $k_{rec}(EJK)$ was superscripted with a plus sign. The first term of Eq. (G3) is

$$\sum_{J'K'} \int_{E_o}^{\infty} Z'(E',E) g(E'J'K')_+ dE' \int_{E_o}^{\infty} Z(E,E') dE'$$
$$= \sum_{J'K'} \int_{E_o}^{\infty} Z_{LJ} Z'(E',E) g(E'J'K')_+ dE'$$
$$= \sum_{J'K'} \int_{E_o}^{\infty} Z(E',E) g(E'J'K')_+ dE'$$

since $Z_{LJ} = \int_{E_o}^{\infty} Z(E,E') dE'$ and $Z(E',E) = Z_{LJ} Z'(E',E)$. Therefore the first and the second terms of the master equation in Eq. (G3), or in Eq. (13), cancel which leaves the third term in Eq. (G3) for consideration.

The third term of the master equation, in Eq. (13) or Eq. (G3), is $k_d(EJK) g(EJK)_+$. Upon using the definition for $g(EJK)_+$ from Eq. (29) and substituting it in $k_d(EJK) g(EJK)_+$ yields

$$k_d(EJK) [\frac{k_r(EJK) A \circ BC}{Z_{LJ} + k_d(EJK)} + k_d(EJK)^{-1} \times \sum_{J'K'} \int_{E_o}^{\infty} \frac{k_r(EJK) A \circ BC \, Z(E,E') dE'}{Z_{LJ} + k_d(E'J'K')}]. \qquad (G4)$$

At the high pressure limit as $Z_{LJ} \to \infty$, then for the first term of Eq. (G4), we have

$$\lim_{Z_{LJ} \to \infty} \frac{k_d(EJK) k_r(EJK) A \circ BC}{Z_{LJ} + k_d(EJK)} = 0.$$

For the treatment of the second term in Eq. (G4), the $k_d(EJK)$ from outside the bracket cancels the $k_d(EJK)^{-1}$ of the second term, and using $Z(E,E') = Z_{LJ} Z'(E,E')$ to explicitly isolate the term Z_{LJ}, the second term may be written as $\sum_{J'K'} \int_{E_o}^{\infty} \frac{k_r(EJK) A \circ BC \, Z_{LJ} Z'(E,E') dE'}{Z_{LJ} + k_d(E'J'K')}$. We now take the high pressure limit of the latter equation by applying the L'Hopital's rule to it to yield

$$\lim_{Z_{LJ} \to \infty} \sum_{J'K'} \int_{E_o}^{\infty} \frac{k_r(EJK) A \circ BC \, Z_{LJ} Z'(E,E') dE'}{Z_{LJ} + k_d(E'J'K')}$$
$$= \sum_{J'K'} \int_{E_o}^{\infty} k_r(EJK) A \circ BC \, Z'(E,E') dE'. \qquad (G5)$$

Since only $Z'(E,E')$ depends on E' in the integrand of Eq. (G5), the right hand side, then $\int_{E_o}^{\infty} Z'(E,E')dE' = 1$ via the completeness requirement of transition probability,[52–54] and Eq. (G5) becomes $\sum_{J'K'} k_r(EJK)A \circ BC$. Finally summing over $(J'K')$ and substituting for $k_r(EJK)$ by noting its definition, from Eq. (7), yield for the bimolecular master equation, at the high pressure limit,[63] to be

$$k_{rec}^{+}(EJK) = N^*(EJK)e^{-E/kT}/hQ, \quad E > E^*(JK) \qquad (G6)$$

upon having canceled $A \circ BC$ from both sides of the equation in Eq. (G6).

We now consider the contribution to $k_{rec}(EJK)$ for the energy region $E \leq E^*(JK)$. We solve Eq. (17) for $g(EJK)_-$, where now $f(EJK) = 0$ in Eq. (17), to yield

$$g(EJK)_- = \frac{\sum_{J'K'} \int_{E_o}^{\infty} Z(E',E)g(E'J'K')_- dE'}{\int_{E_o}^{\infty} Z(E,E')dE' + k_d(EJK)}. \qquad (G7)$$

We again take the high pressure limit, $Z_{LJ} \to \infty$, of Eq. (G7) and upon applying L'Hopital's rule yields

$$g(EJK)_- = \sum_{J'K'} \int_{E_o}^{\infty} Z'(E',E)g(E'J'K')_- dE', \qquad (G8)$$

where $Z(E',E) = Z_{LJ}Z'(E',E)$, and the denominator of Eq. (G7) is unity. Upon inserting $g(EJK)_-$ from Eq. (G8) into the first term of the master equation, Eq. (13), yields a master equation

$$k_{rec}^{-}(EJK)A \circ BC = \sum_{J'K'} \int_{E_o}^{\infty} Z'(E',E)g(E'J'K')_- dE'$$
$$\times \int_{E_o}^{\infty} Z(E,E')dE'$$
$$- \sum_{J'K'} \int_{E_o}^{\infty} Z(E',E)g(E'J'K')_- dE', \qquad (G9)$$

where the third term of Eq. (13) is $k_d(EJK)g(EJK) = 0$, since $k_d(EJK) = 0$ for $E \leq E^*(JK)$, and so absent in Eq. (G9), and the $k_{rec}(EJK)$ was superscripted with a minus sign. The first term of Eq. (G9) is again

$$\sum_{J'K'} \int_{E_o}^{\infty} Z'(E',E)g(E'J'K')_- dE' \int_{E_o}^{\infty} Z(E,E')dE'$$
$$= \sum_{J'K'} \int_{E_o}^{\infty} Z_{LJ}Z'(E',E)g(E'J'K')_- dE'$$
$$= \sum_{J'K'} \int_{E_o}^{\infty} Z(E',E)g(E'J'K')_- dE'$$

since $Z_{LJ} = \int_{E_o}^{\infty} Z(E,E')dE'$ and $Z(E',E) = Z_{LJ}Z'(E',E)$. Therefore the first and the second terms of the master equation

in Eq. (G9) cancel and so

$$k_{rec}^{-}(EJK) = 0, \quad E \leq E^*(JK). \qquad (G10)$$

Thereupon, considering the results for both energy regions for $k_{rec}(EJK)$, from Eqs. (G6) to (G10), shows that the K-adiabatic master equation reduced to the high pressure limit form of RRKM theory[63] at the high pressure limit, which completes the proof. All contributions to the $k_{rec}(EJK)$ arise from the energy region $E > E^*(JK)$ from Eq. (G6).

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[43]A recurrence relation is an equation that expresses a function f_n as some combination of f_i with $i < n$. Once the initial condition(s) are specified, then each further term in the sequence or array is specified as a function of the preceding terms in a recursive manner. The term "difference equation" is also used. For further discussion, please see Refs. 44 and 45.

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[50]In Eq. (27), $f(EJK) > 0$, $\lambda \hat{A} > 0$, and $\lambda_1 \hat{C} > 0$, where necessarily $E > E^*(JK)$ so to have $k_d(EJK) > 0$ to avoid a singularity in $\hat{A}$, and for $k_r(EJK) > 0$ so to have both $\hat{A} > 0$ and $f(EJK) > 0$, where otherwise if $k_d = 0$ then, undesirably, $f(EJK) = 0$, $\hat{A} = 0$, and hence $f(EJK) + \lambda \hat{A} = 0$, so to yield a singularity in the left hand side of Eq. (27).

[51]In this case, $k_d = 0$ and $k_r > 0$. For a given (EJK), it may be assumed that both the associative and dissociative channels are open for energies greater than the critical energy $E^*(JK)$, unless subtle geometric and dynamical effects would render either one open and the other closed to association or recombination for the same (EJK).

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[71]For example, in Ref. 27, the analytic solution (population) from Wiener-Hopf technique was inserted in $\int \int g(E)Z(E', E)dE'dE$ to obtain the low pressure recombination rate constant. The J and K degree of freedoms may be introduced in the latter formula.

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