

# Comment on "A statistical theory of rate constants in nonergodic systems"<sup>a)</sup>

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Nonseparable Hamiltonian systems of two degrees of freedom display a transition to chaos at a particular energy.<sup>1</sup> The four-dimensional phase space of such systems is decomposable into regular and irregular regions, each of finite measure. The regular region is further decomposable into two-dimensional invariant manifolds (or tori). It is of interest to understand the dynamical behavior of systems in which the potential energy surface has a saddle point and is otherwise completely bounded. It is then possible to choose coordinates such that one is a reaction coordinate involving passage from one potential well over the barrier to the other potential well, and the other coordinate is a bounded oscillatory coordinate. In a previous publication,<sup>2</sup> we showed that the coupling between these coordinates could, under certain circumstances, lead to the existence of a unimolecular rate law and concomitantly to the existence of rate constants. The conditions required for this are that the total energy is only slightly larger than the barrier and all the *crossing tori* as well as a measurable set of *trapping tori* must be destroyed. If all tori are destroyed by the coupling; that is, if the system is completely stochastic,<sup>2,3</sup> we found that the rate constants are given by RRKM theory. However, when not all the trapping tori are destroyed, the system is not ergodic. In this case, RRKM theory cannot be valid because it is a tenet of that purely statistical theory that all regions of the energy hypersurface in phase space are accessible to the crossing trajectories—i.e., the system is ergodic.

In our previous publication, we attempted to generalize RRKM theory to the nonergodic case. We showed that if the irregular region of the energy surface contains all crossing trajectories, and if the irregular region is "mixing" in the sense that (a) any trajectory spends equal times in irregular regions of equal microcanonical measure, and (b) the Cartesian distance between initially neighboring trajectories exponentiates, then the chemical relaxation time (or kinetic rate constant) is given by

$$\frac{1}{\tau_{BD}} = \frac{1}{\mu_{irr}} \frac{1}{\tau_{RRKM}}, \quad (1)$$

where  $\mu_{irr}$  is the microcanonical measure of the irregular region of the energy surface, and the RRKM rate constant is

$$\frac{1}{\tau_{RRKM}} = \frac{1}{x_A x_B} \langle \dot{y} \theta(\dot{y}) \delta(y - y_c) \rangle_E, \quad (2)$$

where the terms are defined in Ref. 1. Since  $\mu_{irr} \leq 1$ , it follows that  $1/\tau_{BD} \geq 1/\tau_{RRKM}$ . It is to be understood that the full measure  $\mu$  ( $= \mu_{reg} + \mu_{irr}$ ) is normalized to unity.

In Ref. 2, we gave evidence that when trapping tori exist, the motion in the irregular region is neither ergodic nor mixing. There seem to exist attractors or "vague tori" that cause the trajectories to spend more time in certain regions than in others of equal measure. In this case, the generalized RRKM theory cannot be valid. Recently, we have studied this question anew in different dynamical systems and find that there are cases in which the motion is ergodic and possibly mixing in the irregular region. Then, to compare the observed rate constant with the prediction given in Eq. (1), it is necessary to determine  $\mu_{irr}$ . Because this is generally a difficult quantity to determine, we outline a method for its determination below.

Let  $M$  denote the three-dimensional manifold (for a system of two degrees of freedom) corresponding to the constant energy hypersurface, and let  $T^t$  denote the Hamiltonian flow in this surface.  $T^t$  maps  $M$  into itself  $T^t: M \rightarrow M$ . Let  $N$  denote a two-dimensional manifold—say the  $(x, p_x)$  plane and let  $\phi$  represent the mapping onto this plane that generates the Poincare surface of section  $\phi: N \rightarrow N$ .

According to Piesen's formula,<sup>4,5</sup> the Kolmogorov entropy  $h_\mu(\{T^t\})$ , corresponding to the flow  $T^t$  is related to the Lyapunov characteristic number  $\{\lambda_i^\mu(\Gamma)\}$  by

$$h_i^\mu(\{T^t\}) = \int_M \sum_{\lambda_i(\Gamma) > 0} \lambda_i^\mu(\Gamma) d\mu(\Gamma), \quad (3)$$

where  $\Gamma$  refers to a point in  $M$  and  $d_\mu(\Gamma)$  is the microcanonical measure. If the Hamiltonian is an even function of the momentum, it can be shown that<sup>5</sup>

$$h_\mu(\{T^t\}) = \int_M \lambda_{max}^\mu(\Gamma) d\mu(\Gamma), \quad (4)$$

where  $\lambda_{max}^\mu(\Gamma)$  is the maximal Lyapunov number at  $\Gamma$ . In like manner, the Kolmogorov entropy of  $h_\nu(\{\phi\})$  of the mapping on the Poincare surface can be related to the maximum Lyapunov number  $\{\lambda_{max}^\nu(\gamma)\}$  at the point  $\gamma$  in  $N$  by

$$h_\nu(\{\phi\}) = \int_N \lambda_{max}^\nu(\gamma) d\nu(\gamma), \quad (5)$$

where  $d\nu(\gamma)$  is the measure on  $N$  corresponding to the microcanonical measure on  $M$ .

The Kolmogorov entropies  $h_\nu(\{T^t\})$  and  $h_\nu(\{\phi\})$  are connected through Abamov's formula as follows<sup>6-8</sup>:

$$h_\nu(\{T^t\}) = A^{-1} h_\nu(\{\phi\}), \quad (6)$$

where

$$A \equiv \int_N l(\gamma) d\nu(\gamma), \quad (7)$$

and where  $l(\gamma)$  denotes the "time of first return" of  $\gamma$ ,

i. e., the smallest  $t > 0$  such that  $T^t \gamma \in N$ .

Therefore,

$$\int_M \lambda_{\max}(\Gamma) d\mu(\Gamma) = A^{-1} \int_N \lambda_{\max}^{\nu}(\gamma) d\nu(\gamma). \quad (8)$$

If we now make two assumptions (both well founded numerically)

(i)  $\lambda_{\max}^{\mu}(\Gamma) = \lambda_{\max}^{\mu} = \text{const}$ ;  $\Gamma$  in stochastic region,

(ii)  $\lambda_{\max}^{\nu}(\gamma) = \lambda_{\max}^{\nu} = \text{const}$ ;  $\gamma$  in stochastic region,

and recognize that in the regular region  $\lambda_{\max}^{\mu} = \lambda_{\max}^{\nu} = 0$ , then Eq. (8) reduces to

$$\lambda_{\max}^{\mu} \mu_{\text{irr}} = A^{-1} \lambda_{\max}^{\nu} \nu_{\text{irr}}, \quad (9)$$

where  $\mu_{\text{irr}}$ , and  $\nu_{\text{irr}}$  are the measures of the stochastic regions of the  $M$  and  $N$  manifolds, respectively. Thus,

$$\mu_{\text{irr}} = A^{-1} \left( \frac{\lambda_{\max}^{\nu}}{\lambda_{\max}^{\mu}} \right) \nu_{\text{irr}}. \quad (10)$$

Substitution into Eq. (1) then gives the rate constant

$$\frac{1}{\tau_{BD}} = A \left( \frac{\lambda_{\max}^{\mu}}{\lambda_{\max}^{\nu}} \right) \frac{1}{\nu_{\text{irr}}} \frac{1}{\tau_{RRKM}}. \quad (11)$$

Now, it is a routine matter to numerically determine  $A$ ,  $\lambda_{\max}^{\mu}$ ,  $\lambda_{\max}^{\nu}$ , and  $\nu_{\text{irr}}$  from trajectories in  $M$  and from the Poincare surface of section.

Recently, it has been shown that in some systems the irregular region is further decomposable into bands of stochasticity,<sup>7,9</sup> each with different Lyapunov numbers

(constant on each band) and with different corresponding Kolmogorov entropies. It is possible to generalize the foregoing to this case. Let  $1/\tau_{BD}(i)$  denote the rate constant for the  $i$ th stochastic band. If this contains crossing trajectories, then

$$\frac{1}{\tau_{BD}(i)} = \frac{1}{\mu_{\text{irr}}(i)} \frac{1}{\tau_{RRKM}}, \quad (12)$$

where  $\mu_{\text{irr}}(i)$  is the microcanonical measure of this band to be determined as above. It is important to note that there can now be a wide distribution of values of the rate constant corresponding to the different bands so that the reactive flux will not behave exponentially, but rather as a superposition of exponentials.

<sup>1</sup>M. Henon and C. Heils, *Astron. J.* **69**, 73 (1964).

<sup>2</sup>N. De Leon and B. J. Berne, *J. Chem. Phys.* **75**, 3495 (1981).

<sup>3</sup>N. De Leon and B. J. Berne, *J. Chem. Phys.* (to be published).

<sup>4</sup>Ya B. Piesin, *Dokl. Akad. Nauk. SSSR* **226**, 774 (1976), [*Soviet Math. Dokl.* **17**, 196 (1976).]

<sup>5</sup>G. Benettin, L. Galgani, and J. M. Strelcyn, *Phys. Rev. A* **14**, 2338 (1976).

<sup>6</sup>M. Casartelli, E. Drana, L. Galgani, and A. Scotti, *Phys. Rev. A* **13**, 1921 (1976).

<sup>7</sup>G. Benettin and J. M. Strelcyn, *Phys. Rev. A* **17**, 773 (1977).

<sup>8</sup>L. M. Abamov, *Dokl. Akad. Nauk. SSSR* **128**, 973 (1959). [English translation in *Am. Math. Soc. Trans.* **49**, 167 (1966).]

<sup>9</sup>M. C. Carotta, C. Ferrario, G. Lo Vecchio, and L. Galgani, *Phys. Rev. A* **17**, 786 (1978).

## On the existence of sulfur superoxide and its formation in the combustion of carbon disulfide

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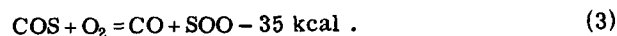
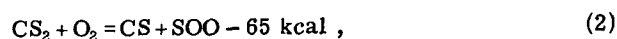
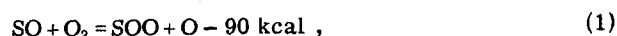
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Approximately 25 years ago, the sulfur superoxide isomer SOO was first postulated by Myerson, Taylor, and Hans<sup>1</sup> (MTH), to explain an absorption continuum (210 to >300 nm) observed during CS<sub>2</sub>-O<sub>2</sub> and COS-O<sub>2</sub> explosions. Shortly thereafter, a similar continuum was noted<sup>2,3</sup> in flash photolysis studies of H<sub>2</sub>S combustion first by Norrish and Zeelenberg<sup>2</sup> and then by Norrish and Oldershaw,<sup>3</sup> who agreed that the studies indicated an isomer but one of unknown structure. Since then at least 14 papers have debated SOO's existence and its role as the continuous absorber (c.a.), subsequently replaced by SO<sub>2</sub> spectra. We shall show that the concepts of the original paper<sup>1</sup> still maintain their integrity.

A recent paper by Dunning and Raffanetti<sup>4</sup> (DR) presents calculations of the equilibrium geometries and isomerization energies of the three isomers of SO<sub>2</sub>: (1) the superoxide SOO, (2) the ring isomer, and (3) the normal open isomer (sic). The work clearly predicts a stable SOO, in accord with our own postulation.

However, DR infer from their data that the continuous absorption observed by MTH is not likely to be SOO and that some of the MTH reactions postulated for its formation are improbable. We would like to offer corrections to these inferences and comment on a few of the most pertinent of the other papers.

The calculations performed by DR are certainly assumed to be reliable. However, their application to the participation of SOO in the oxidation of S compounds is not acceptable. Three of the important reactions which MTH believe responsible for SOO production were questioned on the basis of the endoergicities and lack of spin conservation:



It must be realized that a classical, fully corrobo-