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Vibrational Energy Transfer and Relaxation in O_2 and H_2O[†]

David L. Huestis*

Molecular Physics Laboratory, SRI International, Menlo Park, California 94025

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Near-resonant vibrational energy exchange between oxygen and water molecules is an important process in the Earth's atmosphere, combustion chemistry, and the chemical oxygen iodine laser (COIL). The reactions in question are (1) $O_2(1) + O_2(0) \rightarrow O_2(0) + O_2(0)$; (2) $O_2(1) + H_2O(000) \rightarrow O_2(0) + H_2O(000)$; (3) $O_2(1) + H_2O(000) \leftrightarrow O_2(0) + H_2O(010)$; (4) $H_2O(010) + H_2O(000) \rightarrow H_2O(000) + H_2O(000)$; and (5) $H_2O(010) + O_2(0) \rightarrow H_2O(000) + O_2(0)$. Reanalysis of the data available in the chemical kinetics literature provides reliable values for rate coefficients for reactions 1 and 4 and strong evidence that reactions 2 and 5 are slow in comparison with reaction 3. Analytical solution of the chemical rate equations shows that previous attempts to measure the rate of reaction 3 are unreliable unless the water mole fraction is higher than 1%. Reanalysis of data from the only experiment satisfying this constraint provides a rate coefficient of $(5.5 \pm 0.4) \times 10^{-13}$ cm^3/s at room temperature, between the values favored by the atmospheric and laser modeling communities.

Introduction

Vibrational energy transfer and relaxation in gases are extensively investigated subjects of importance in many applications. The primary focus of this investigation is on the Earth's stratosphere and mesosphere at altitudes between 40 and 110 km, where vibrational energy transfer from oxygen molecules to water molecules helps control the local temperature through infrared radiative cooling and must be quantitatively understood to retrieve the water altitude profile from infrared radiance.[1−3] A secondary application is modeling of the chemical oxygen iodine laser (COIL), now under development by the U.S. Air Force[4] and international research teams,[5,6] where $O_2(a^1\Delta_g)$ is generated in aqueous solution. Additional information is available from combustion chemistry, where O_2 is a primary reagent, and H_2O is a primary product.[7−9] The reactions in question are

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

$$O_2(1) + H_2O(000) \rightarrow O_2(0) + H_2O(000) \qquad (2)$$

$$O_2(1) + H_2O(000) \leftrightarrow O_2(0) + H_2O(010) \qquad (3)$$

$$H_2O(010) + H_2O(000) \rightarrow H_2O(000) + H_2O(000) \qquad (4)$$

$$H_2O(010) + O_2(0) \rightarrow H_2O(000) + O_2(0) \qquad (5)$$

The need for critical evaluation of the available information is illustrated by the fact that the atmospheric science and laser modeling communities use significantly different rate coefficients for some of these reactions and only recently became aware of each other's efforts. For example, both communities consider the rate of reaction 3 to be one of the key parameters, yet the atmospheric science community[1] favors a relatively large value of 1.7×10^{-12} cm^3/s [actually the reverse reaction (−3)], while the Russian laser modelers[5] favor a much smaller value of 3×10^{-13} cm^3/s. In both cases, the complexity of the models and the limited laboratory experimental data provide weak constraints. In the following analysis, we will use unpublished data from the combustion diagnostics community[7,8] to provide recommended values and temperature dependence with assigned uncertainty estimates.

Similarly, we provide the first critical evaluation of the information on reaction 1 that is available in the literature from high-temperature shock-tube studies,[10−12] moderate-temperature ultrasound absorption,[13−15] and anti-Stokes Raman scattering in liquid oxygen,[16−20] as well as accurate chemical dynamics calculations.[21] We also reanalyze the temperature dependence of reaction 4[22] and conclude that there is no quantitative basis for estimating the rates of reactions 2 and 5, but they should be small enough to be ignored in laboratory kinetics experiments, given the estimated magnitudes and uncertainties in the rates of reactions 1, 3, and 4.

Analysis

VV Energy Exchange in Pure Oxygen and Pure Water Vapor. It is generally assumed[23] that near-resonant vibration−vibration energy exchange is much faster than VT vibrational relaxation. For example, two recent measurements[9,24] of the rate of the reactions

$$O_2(v) + O_2(0) \leftrightarrow O_2(v-1) + O_2(1)$$

suggest rate coefficients of about 3×10^{-13} cm^3/s for $v = 2$ and 3, five orders of magnitude faster that VT relaxation (discussed next). Thus, we can safely assume that under most conditions, the vibrational energy in $O_2(v)$ is rapidly redistributed to establish an effective vibrational temperature, which means that most of the population will be found in $v = 0$ and 1. Similarly, we wish to assume that the population in $H_2O(0v0)$ is rapidly equilibrated

$$H_2O(020) + H_2O(000) \leftrightarrow H_2O(010) + H_2O(010)$$

However, the two previous laboratory investigations[22,25] suggest

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* Corresponding author. E-mail: david.huestis@sri.com. Phone: (650) 859-3464. Fax: (650) 859-6196.

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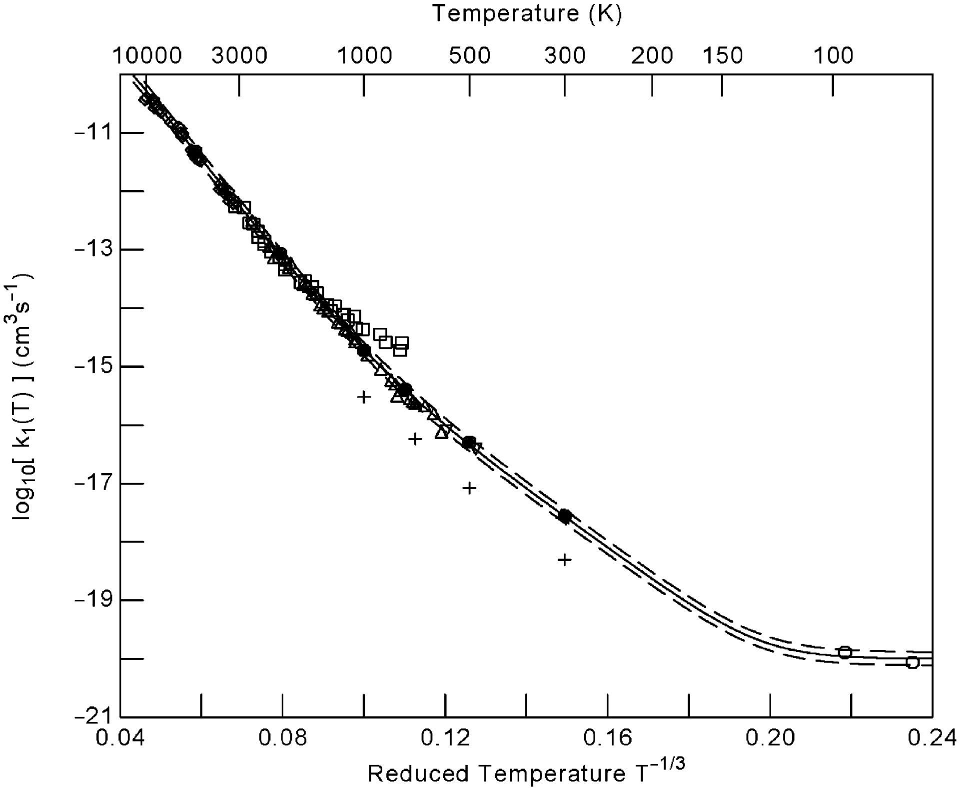

Figure 1. VT vibrational relaxation of $O_2(1)$ in collisions with O_2: reaction 1. Shock tube experiments: □,[10] ◇,[11] and △.[12] Sound absorption: ▽,[15] plus two measurements[13,14] at 300 K that are masked by the overlapping ● symbol. Quasi-classical trajectory theory: ●[21] and +.[26] Anti-Stokes Raman scattering in liquid oxygen (divided by two): ○.[16,17] Current parametrization: solid line = fit and dashed lines = ±30% confidence limits.

that while the population in $H_2O(020)$ decays twice as fast as that in $H_2O(010)$, the relative yield of $H_2O(010)$ and $H_2O(000)$ is not quantitatively established.

VT Relaxation in Pure Oxygen. It is surprising that no critical evaluation has been published that reanalyzes the wealth of information available on reaction 1 from measurements using ultrasound absorption,[13−15] shock tubes,[10−12] and anti-Stokes Raman scattering in liquid oxygen,[16−20] as well as accurate chemical dynamics calculations.[21] Figure 1 illustrates our analysis of the temperature dependence of the rate coefficient for VT vibrational relaxation in oxygen, which is summarized by the empirical formula

$$k_1(T) = 1 \times 10^{-20} + 7.7 \times 10^{-11} \exp(-115/T^{1/3}) + 5.3 \times 10^{-7} \exp(-199/T^{1/3})\ \mathrm{cm^3/s}$$

in which all the numerical constants were adjusted to give the best fit to the point symbols in Figure 1. The fit was biased in favor of the high-quality quasi-classical trajectory calculations of Billing and Kolesnick,[21] which are quantitatively consistent with the body of experimental data. Note that the results from the room-temperature sound absorption experiments[13,14] are masked by the overlapping ● symbols. In appears clear that the earliest shock-tube measurements,[10] indicated by □ symbols in Figure 1, are unreliable at lower temperatures. We also conclude that the potential surface used for the most recent quasi-classical trajectory studies,[26] indicated by + symbols in Figure 1, is less reliable than that used in the earlier studies,[21] indicated by ● symbols in Figure 1. Ahn et al.[9] found that the Coletti and Billing[26] rate coefficients for VV transfer were also too small by about an order of magnitude. We estimate the $1-\sigma$ confidence limit in the determination of $k_1(T)$ as 30% above 300 K, 15% at 300 K, 30% at 200 K, and a factor of two below 100 K. Thus, we recommend

$$k_1(300) = (2.7 \pm 0.4) \times 10^{-18}\ \mathrm{cm^3/s}$$

$$k_1(200) = (2.3 \pm 0.7) \times 10^{-19}\ \mathrm{cm^3/s}$$

Additional measurements between 150 and 300 K are clearly needed.

The functional form of the exponential terms is motivated by the Landau−Teller theory of vibrational relaxation.[27−29] The $\exp(-T^{-1/3})$ dependence results from a Boltzman average of a cross section that varies as $\exp(-E^{-1/2})$, which is the form expected for a one-dimensional hard collision that releases a large amount of translational energy.

The first temperature-independent term corresponds to the observed rate of vibrational relaxation in liquid oxygen[16,17] but is scaled downward by a factor of 2 based on the observation[30] that the rate coefficients for electronic relaxation are faster in liquid oxygen than in gaseous oxygen at the same temperature. The second two exponential terms can be thought of as corresponding to two more vibrational relaxation mechanisms that are effective at higher collision energies. We could speculate that the first or low-temperature mechanism corresponds to vibrational relaxation mediated by electron spin, considering that collisional vibrational relaxation in liquid nitrogen is estimated to be about a factor of 10^5 slower.[20] The high-temperature mechanism could correspond to the hard-collision vibration-to-translation (VT) model developed originally,[27,28] while the middle-temperature mechanism might correspond to vibration-to-rotation (VR) energy transfer.[29]

Turning to the atmospheric and laser modeling literature, we find that Lopez-Puertas et al.[1] used

$$k_1(T) = 4.2 \times 10^{-19}\,(T/300)^{1/2}\ \mathrm{cm^3/s}$$

citing a paper Parker and Ritke,[31] which is a high-pressure study at 10−110 atm that should not be trusted because extrapolation of their rate coefficients to pressures below 1 atm does not agree with other determinations. In 2001, Azyazov et al.[5] used a value that is almost 5 times larger at room temperature

$$k_1(300) = 2 \times 10^{-18}\ \mathrm{cm^3/s}$$

in rough agreement with the our value stated previously and with that cited by Bass and Shields,[32] but surprisingly citing a different Parker and Ritke publication,[33] which is actually an investigation of relaxation of $O_2(a^1\Delta_g,\ \upsilon = 0, 1)$ in collision with ground-state O_2. Further surprises come in the 2003 publication of Antonov et al.[6], in which we find

$$k_1(300) = 8.2 \times 10^{-19}\ \mathrm{cm^3/s}$$

citing the earlier Parker and Ritke reference[31] for the new number.

VT Relaxation in Pure Water Vapor. Rate coefficients for VT/R vibrational relaxation of $H_2O(010)$ have been adequately determined by the laser-induced fluorescence experiments of Zittel and Masturzo.[22] Our reanalysis is illustrated in Figure 2, which results in

$$k_4(300) = (5.1 \pm 0.5) \times 10^{-11}\ \mathrm{cm^3/s}$$

$$k_4(200) = (5.0 \pm 0.6) \times 10^{-11}\ \mathrm{cm^3/s}$$

Earlier experiments[25] suggest a lower limit of

$$k_4(300) \geq 5.5 \times 10^{-11}\ \mathrm{cm^3/s}$$

The results of both of these experiments are subject to additional uncertainty due to kinetic complexity resulting from initial excitation of $H_2O(100)$ and $H_2O(001)$ rather than direct laser excitation of $H_2O(010)$.

VV Energy Transfer between $O_2(1)$ and $H_2O(010)$. The fact that $O_2(1)$ and $H_2O(010)$ have nearly the same excitation energy is the basis for the supposition that the corresponding VV rate coefficients, k_3 and k_{-3}, must be large. Estimates in the literature cover the range from 3×10^{-13} (ref 5), 1.2×10^{-12} (ref 3), 1.5×10^{-12} (ref 32), and 1.7×10^{-12} (ref 1), to 8.9×10^{-12} (ref 34) cm³/s. Rate coefficients for nonresonant VT/R relaxation of vibrational energy in reactions 2 and 5 are expected to be much slower and may be difficult to determine in the presence of the much faster reaction 3. From their acoustic energy absorption experiments, Bass and Shields[32] suggest $k_2 = 4 \times 10^{-15}$ and $k_4 = 4 \times 10^{-14}$ cm³/s.

We write the coupled differential equations for the time dependence of $O_2(1)$ and $H_2O(010)$ for reactions 1−5 as

$$(\mathrm{d}/\mathrm{d}t)[O_2(1)] = -\alpha[O_2(1)] + \beta[H_2O(010)]$$

$$(\mathrm{d}/\mathrm{d}t)[H_2O(010)] = \gamma[O_2(1)] - \delta[H_2O(010)]$$

where

$$\alpha = k_1[O_2(0)] + (k_2 + k_3)[H_2O(000)]$$

$$\beta = k_{-3}[O_2(0)]$$

$$\gamma = k_3[H_2O(000)]$$

$$\delta = (k_{-3} + k_5)[O_2(0)] + k_4[H_2O(000)]$$

Under the assumption that $[O_2(0)]$ and $[H_2O(000)]$ can be taken to be time independent (i.e., that the effective vibrational temperatures are not too high), we can take α, β, γ, and δ as constants for any specific experiment, and then we solve the differential equations analytically, obtaining

$$[O_2(1)](t) = A\exp(-\lambda(\mathrm{fast})t) + B\exp(-\lambda(\mathrm{slow})t)$$

$$[H_2O(010)](t) = C\exp(-\lambda(\mathrm{fast})t) + D\exp(-\lambda(\mathrm{slow})t)$$

where λ(fast) and λ(slow) are calculated from the two roots of the eigenvalue equation

$$(\lambda - \alpha)(\lambda - \delta) - \beta\gamma = 0$$

resulting in

$$\lambda(\mathrm{fast}) = 1/2(\alpha + \delta) + [1/4(\alpha - \delta)^2 + \beta\gamma]^{1/2}$$

$$\lambda(\mathrm{slow}) = (\alpha\delta - \beta\gamma)/\lambda(\mathrm{fast})$$

A similar analysis is provided by Henderson et al.[35] A more complete description would include the expected thermal equilibrium values of $[O_2(1)]$ and $[H_2O(010)]$, but the conclusions derived here about time dependence would be unchanged. The time dependencies of both $[O_2(1)]$ and $[H_2O(010)]$ are thus described by double exponentials, with an initially excited level decaying at first fast and then slow, while an initally unexcited level would rise quickly and decay slowly, as reflected in the coefficients A−D as defined by the initial excitation conditions.

Using the expected relative magnitudes of the rate coefficients

$$k_1 << k_2, k_5 << k_3 \approx k_{-3} << k_4$$

we can develop working approximations values for λ(fast) and λ(slow) for various experimental conditions.

In the case of an experiment in which $H_2O(010)$ is excited with a short-duration infrared laser, we should be able to measure λ(fast), which we would approximate as

$$\lambda(\mathrm{fast}) \approx k_{-3}[O_2] + k_4[H_2O]$$

from which we could derive k_{-3} by varying the O_2 pressure. Such an experiment would be similar to that performed by Finzi et al.,[25] but they excited the $H_2O(100/001)$ levels, which made kinetics analysis much more complicated. Those experiments should be repeated with direct laser excitation of the $H_2O(010)$ level.

Another approach is to monitor the decay of the overall vibrational energy in $O_2(1)$ plus $H_2O(010)$, through the pressure dependence of λ(slow). Such an experiment was performed by Diskin.[7,8] Population in $O_2(1)$ is created by stimulated Raman scattering using two lasers differing in frequency by the O_2 vibrational quantum energy. The time evolution of the $O_2(1)$ population is observed by VUV laser-induced fluorescence through the $O_2(B^3\Sigma_u^-)$ state. In Diskin's experiments, at elevated temperatures the water density was large enough such that $k_4[H_2O] \gg k_{-3}[O_2]$, which is the requirement that reaction 4 is sufficiently fast enough that reaction 3 becomes the rate-determining step. In this case, we can show that

$$\lambda(\mathrm{slow}) \approx k_3[H_2O]$$

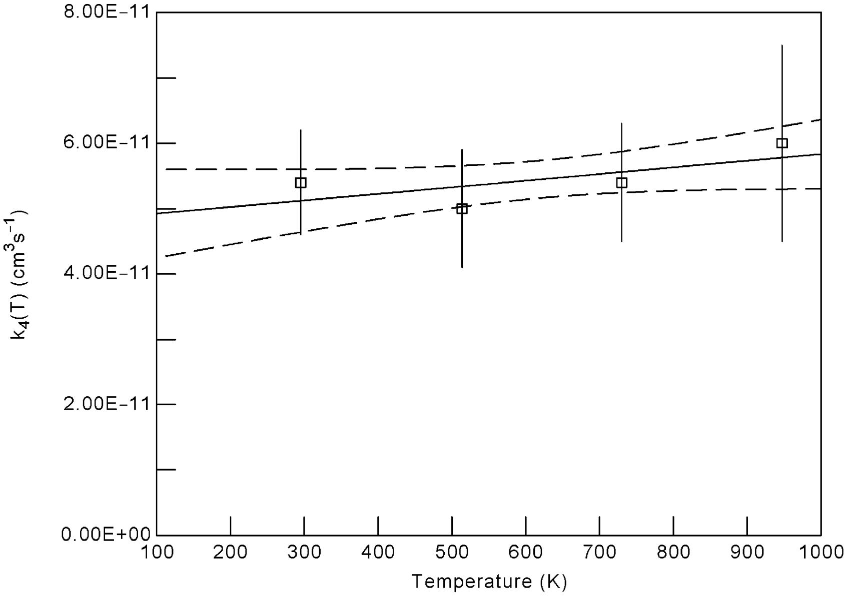

Figure 2. VT/R vibrational relaxation of $H_2O(010)$ in collisions with H_2O: reaction 4. Laser-induced fluorescence: □ = nominal values and vertical lines = $1 - \sigma$ uncertainties from Zittel and Masturzo.[22] Current parametrization: solid line = fit and dashed lines = statistical $1 - \sigma$ confidence limits.

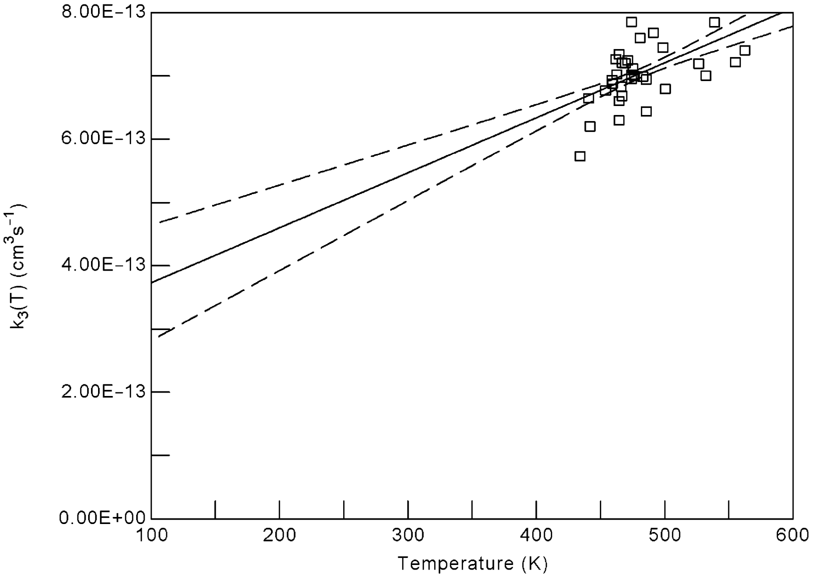

Figure 3. Vibrational energy transfer from $O_2(1)$ to H_2O: reaction 3. Stimulated Raman excitation of $O_2(1)$: □.[7,8] Current parametrization: solid line = fit and dashed lines = statistical $1 - \sigma$ confidence limits.

Figure 3 shows the results of our reanalysis of Diskin's data assuming that k_3 has linear temperature dependence. His assumption of a $T^{1/2}$ dependence is plausible but cannot be enforced by his measurement uncertainties. We recommend

$$k_3(300\ \text{K}) = (5.5 \pm 0.4) \times 10^{-13}\ \text{cm}^3/\text{s}$$

$$k_3(200\ \text{K}) = (4.6 \pm 0.7) \times 10^{-13}\ \text{cm}^3/\text{s}$$

with linear temperature interpolation of values and uncertainties. The assigned $1 - \sigma$ statistical uncertainties are large (perhaps even underestimates) because of the scatter in the data and the long extrapolation from the temperature range of the measurements (430−570 K), but they are much smaller than those from previous determinations.[32,34] Note that most of the earlier measurements were performed at water mole fractions well below the 1% lower limit imposed by our kinetics analysis. As a result, much more complicated modeling would be required to extract reliable rate coefficients from experiments of the type performed previously. Henderson et al.[35] and Monk[36] show that the decay rates observed in sound absorption vary quadratically in the water mole fraction below 1%.

VT Relaxation of $O_2(1)$ by H_2O and $H_2O(010)$ by O_2. As noted earlier in this Article, the values of k_2 and k_5 were only weakly constrained in previous work.[32,34] It is not obvious how to design experiments to measure them accurately in the presence of the much faster VV energy transfer reaction 3.

Conclusions

Here, we have presented a reanalysis and critical evaluation of the data available in the literature on vibrational energy transfer and relaxation in oxygen and water molecules. This evaluation provides recommended rate coefficients with believable uncertainty estimates for use in modeling the kinetics of the atmosphere, chemical lasers, and combustion.

This work represents an example output from a proposed long-term program of critical evaluation by domain experts of the rates and cross sections for atomic and molecular processes that are needed for understanding and modeling the atmospheres in the solar system.[37] We envision data products resembling those of the JPL/NASA Panel for Data Evaluation and the similar efforts of the international combustion modeling community funded by U.S. DoE and its European counterpart.

The major topic areas would include the following: (1) chemical reactions of neutral atoms and molecules in their ground electronic states. (2) Ion−molecule reactions. (3) Chemistry, relaxation, and radiation of electronically excited atoms and molecules. (4) Vibrational and rotational relaxation and radiation. (5) Photoabsorption, photodissociation, and photoionization. (6) Electron-impact excitation, dissociation, ionization, and recombination. (7) Energetic heavy particle excitation and charge exchange.

Acknowledgment. This manuscript is dedicated as a memorial to Prof. Gert D. Billing and as a celebration of the 70th birthday of Dr. David M. Golden, both valued colleagues of the author. Gert Billing was a pioneer in developing theoretical techniques for the calculation of cross sections and rates for vibrational energy exchange and relaxation, which requires balanced treatment of the quantum mechanical nature of high-frequency vibrations with the nearly classical rotational and translational motions of the colliders. Dave Golden's numerous contributions to the field of chemical kinetics represent a nearly ideal combination of (1) knowledge of the literature, (2) insight to identify the central mechanistic questions, (3) skill in designing the best experiments and interpreting the results, (4) development and use of theoretical tools and models, and (5) most importantly, intuitive judgment of what makes sense and what must be in error. Dave Golden's decades-long service on the JPL/NASA Data Evaluation Panel provides inspiration and guidance for the analysis and evaluation presented in this manuscript and for the proposed extension and continuation described previously. This work was supported in part by grants from the Geospace and Planetary Atmospheres programs of the NASA Exploration Science Directorate.

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