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Critical Evaluation of Chemical Reaction Rates and Collision Cross Sections of Importance in the Earth's Upper Atmosphere and the Atmospheres of Other Planets, Moons, and Comets

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ABSTRACT

We propose to establish a 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. 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 US DoE and its European counterpart.

1. The Need for Critical Evaluation

Modelers in all disciplines prefer that the underlying physical and chemical parameter values in their models, the "material properties," would be accurately known in advance and accessible from a computer-readable on-line database of "trusted" values. What is needed is not just a list of processes and numbers (i.e. a "database"), but also documentation of serious critical evaluation of the available information and specific statements from independent expert laboratory/theory data providers about what should be believed, what uncertainty to assign, and what is most in need of redetermination.

2. Topic Areas

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

We envision a gradual progression through the most important microscopic processes in each of the Topic Areas, making maximum use of existing and forthcoming evaluations, reviews, tabulations, and databases. The process should be ongoing, to keep up with developments in the laboratory and to tackle newly discovered needs.

3.   Evaluation Example in Topic 2: Ion-Molecule Reactions $H^+ + H_2$
Ion-Molecule Reactions in the Ionospheres of the Outer Planets

For the past 30 years, models of outer planet ionospheres have used estimated rate coefficients for charge transfer Reaction (1), which is a critical step in controlling the electron density. No confirmation has been available from the laboratory or theory.

$$H^+ + H_2(v \geq 4) \quad \rightarrow \quad H + H_2^+ \tag{1}$$
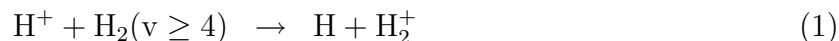
By analysis and extrapolation of the results from recent theoretical work from the plasma fusion community we suggest that Reaction (1) has a rate coefficient of approximately 1.3×10^{-9} cm^3/s, consistent with numbers in current models. In addition we suggest that vibrational relaxation Reaction (2) will also be fast, with rate coefficients of approximately 1.5×10^{-9} cm^3/s for v = 4–8 and 2.8×10^{-9} cm^3/s for v = 1–3. Inclusion of Reaction (2) will significantly reduce calculated vibrational temperatures in ionospheric models. New quantum dynamics calculations are needed.
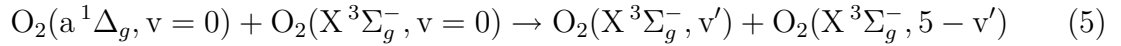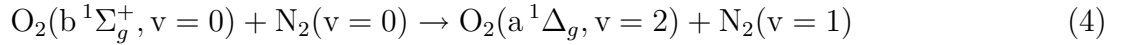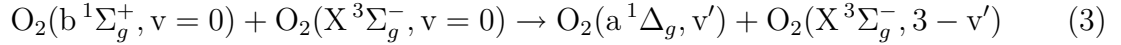
$$H^+ + H_2(v_i) \quad \rightarrow \quad H^+ + H_2(v_f < v_i) \tag{2}$$
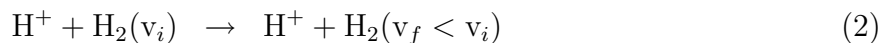
4.   Evaluation Example in Topic 3: Kinetics of Excited Electronic States
Rates and Products of Collisional Relaxation of $O_2(a\,^1\Delta_g)$ and $O_2(b\,^1\Sigma_g^+)$

The low-lying excited states of molecular oxygen, $O_2(a\,^1\Delta_g)$ and $O_2(b\,^1\Sigma_g^+)$, are produced directly or indirectly after absorption of ultraviolet solar radiation in the atmospheres of Venus, Earth, and Mars. At high altitudes, both are weakly quenched and produce strong airglow emission at 1270 nm (Venus, Earth, and Mars) and 762 nm (Earth), respectively. At
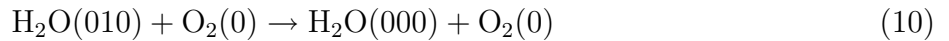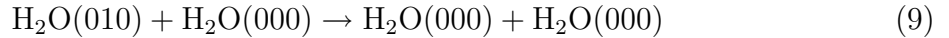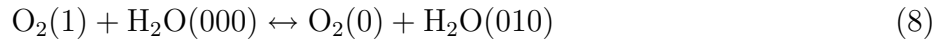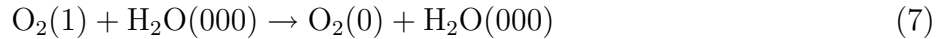
lower altitudes collisional relaxation produces vibrationally excited oxygen molecules in the ground electronic state, which can result in observable infrared emission after vibrational energy transfer to H_2O or CO_2.

Analysis of published kinetics experiments in gaseous and liquid, normal and isotopic oxygen, with or without added nitrogen, allows us to construct functional forms for the temperature dependence of the relaxation rates. In addition, the reactions below illustrate the conclusion relaxation of $O_2(a\,^1\Delta_g)$ and $O_2(b\,^1\Sigma_g^+)$ eventually produces 5 and 8 vibrational quanta, respectively.

$$O_2(b\,^1\Sigma_g^+, v = 0) + O_2(X\,^3\Sigma_g^-, v = 0) \rightarrow O_2(a\,^1\Delta_g, v') + O_2(X\,^3\Sigma_g^-, 3 - v') \qquad (3)$$

$$O_2(b\,^1\Sigma_g^+, v = 0) + N_2(v = 0) \rightarrow O_2(a\,^1\Delta_g, v = 2) + N_2(v = 1) \qquad (4)$$

$$O_2(a\,^1\Delta_g, v = 0) + O_2(X\,^3\Sigma_g^-, v = 0) \rightarrow O_2(X\,^3\Sigma_g^-, v') + O_2(X\,^3\Sigma_g^-, 5 - v') \qquad (5)$$

5. Evaluation Example in Topic 4: Vibrational and Rotational Relaxation and Radiation Vibrational Energy Transfer and Relaxation in O_2 and H_2O

Vibrational energy transfer from oxygen molecules to water molecules helps control the local temperature in the mesosphere through radiative cooling. The reactions in question are

$$O_2(1) + O_2(0) \rightarrow O_2(0) + O_2(0) \qquad (6)$$

$$O_2(1) + H_2O(000) \rightarrow O_2(0) + H_2O(000) \qquad (7)$$

$$O_2(1) + H_2O(000) \leftrightarrow O_2(0) + H_2O(010) \qquad (8)$$

$$H_2O(010) + H_2O(000) \rightarrow H_2O(000) + H_2O(000) \qquad (9)$$

$$H_2O(010) + O_2(0) \rightarrow H_2O(000) + O_2(0) \qquad (10)$$

The chemical kinetics literature provides reliable values for the rates of Reactions (6) and (9) and strong evidence that Reactions (7) and (10) are slow in comparison with Reaction (8). Our analytical solution to the chemical reaction system above shows that the rate of Reaction

(8) can only be measured with water mole fractions higher than 1%. The only measurement that satisfies this requirement is reported in a Ph.D. thesis and a conference presentation from the combustion community. Reanalysis of that data yields our recommended value of $(5.5 \pm 0.4) \times 10^{-13}$ cm^3/s, between the values favored by the atmospheric and laser modeling communities.

6. Evaluation Example in Topic 5: Photoabsorption, Photodissociation, and Photoionization Cross Sections and Yields of O(^{1}S) and O(^{1}D) in Photodissociation of H$_2$O and CO$_2$

A number of observers have used the relative strengths of the oxygen O(^{1}S $\rightarrow$ ^{1}D) *green* and O(^{1}D $\rightarrow$ ^{3}P) *red* lines make inferences about cometary composition. The key questions are the yields of O(^{1}S) and O(^{1}D) in photodissociation of H$_2$O and CO$_2$ by solar radiation. We find that the secondary references used by the cometary community are not mutually consistent and not sufficiently detailed about how the yields were derived from convolution of the solar spectrum with photodissociation yield spectra. After a careful review of the laboratory literature we have concluded that

1. Production of O(^{1}S) by photodissociation of H$_2$O has never been reported in the laboratory literature. In fact, no experiment has been attempted that could have detected production of O(^{1}S). Thus there is no experimental basis for an estimate of its yield.

2. The situation is almost reversed for photodissociation of CO$_2$. The yield of O(^{1}S) has been measured in a number of studies to approach unity in a narrow wavelength window around 112.5 nm. The yield of O(^{1}D) has never been measured (very difficult because of rapid quenching). However, all photochemists believe that it is the primary product over much of the absorption spectrum.

3. Additional experimental yield determinations are needed with high spectral resolution.