LABORATORY STUDIES OF OH VIBRATIONAL RELAXATION BY CARBON DIOXIDE AT MARTIAN TEMPERATURES. R. A. Copeland, Z. M. Geballe, G. P. Smith, and K. S. Kalogerakis, SRI International, Molecular Physics Laboratory, 333 Ravenswood Avenue, Menlo Park, California 94025, email: richard.copeland@sri.com

Introduction: Missions to Mars will be part of America’s space program for decades. While the exact structure of the program is still open to discussion, clearly numerous missions will occur, and planetary researchers will have the opportunity to study the atmosphere of Mars in a level of detail previously reserved exclusively for terrestrial investigations. To prepare for these opportunities and assist in the justification and design of atmospheric science mission instruments, we began a laboratory effort to quantify and characterize what we predict will be among the intense nightglow emission sources in the Martian atmosphere, namely vibrationally excited OH. Intimately connected with water on Mars, the intense infrared emitter OH can potentially monitor atmospheric changes, circulation and gravity waves, and atmospheric composition, density, and local temperature. Such measurements are used routinely to characterize the Earth’s atmosphere.

The presence of water and ozone in the Martian atmosphere suggests that we consider what can be predicted by analogy with the Earth’s nightglow. Emission from OH in the Meinel ground-state vibrational-band system is one of the most prominent features in the terrestrial nightglow. This system covers the spectral range 500–2000 nm, with the strongest bands in the infrared above 1 micron. Estimates of the total band intensity range from 0.6 to 4.5 MR. The source of this emission is the reaction between H atoms and O$_3$ that generates O$_2$ and OH($\nu$ = 6-9). The nascent vibrational distribution extends up to the thermodynamic limit for this very exothermic reaction. The $\nu$ = 6-9 OH molecules then relax to lower vibrational levels, and ultimately the lower levels carry the strongest emission bands in the Earth’s atmosphere.

Models for the intensity and spectral distribution of the OH emission require detailed kinetic information on the collisional relaxation of OH with CO$_2$ at the temperature of the atmosphere of Mars. In 2005, García Muñoz et al. [1] published a model incorporating the best available laboratory data. A significant fraction of the laboratory data was measured in our laboratory at SRI [2-6] and the rest was measured at AFRL [7]. Unfortunately, all the experimental data for CO$_2$ was at room temperature except for an SRI investigation for $\nu$ = 10 [8] and significant gaps existed in the vibrational level dependence of the rate constants.

In this work, we report on two laser-based experiments. The first measures the temperature dependence of the removal rate constant for OH in $\nu$ = 3 and 4 with CO$_2$ while the second confirms SRI’s earlier measurement of the collisional removal rate constant for OH($\nu$ = 9) with CO$_2$ [2].

Experimental Approach and Results: The general experimental approach in this work uses the nanosecond pulse (248 nm) from a KrF excimer laser to photodissociate ozone in an O$_2$/H$_2$/CO$_2$/N$_2$ mixture and a second laser pulse to probe the vibrationally excited OH that is chemically produced in this mixture by laser-induced fluorescence (LIF). By changing the relative gas composition collisional energy transfer rate constants can be extracted.

OH($\nu$ = 3 and 4) low temperature experiments. We understand the system extremely well based on previous SRI studies of OH removal by O atoms [9]. In this system, a small fraction of the O($^1P$) reacts with H$_2$ generating a small quantity of vibrationally excited OH, before being deactivated to O($^3P$) by either the N$_2$ or CO$_2$. The vibrationally excited OH is then collisionally deactivated by the species in the system. The major species, N$_2$, is extremely slow at relaxing OH($\nu$), [10] and the other species will be present at much lower concentrations than CO$_2$. By following the intensity of the LIF versus the time delay between the photolysis laser pulse and the probe dye laser pulse, we monitor the time evolution of OH($\nu$ = 3 and 4) determining the effect of collisions with CO$_2$. By fitting the experimental data to a single exponential, we can extract the collisional removal by CO$_2$. From the shape of the OH($\nu$ = 3) signal, we can estimate the amount of collisional cascading from $\nu$ = 4 to $\nu$ = 3. Measurements with CO$_2$ collider have been performed from room temperature down to 170 K. The signals in this system are large and are yielding very accurate rate constants. To prevent O-atom collisions from affecting the CO$_2$ results, we work at low ozone pressure and high CO$_2$ pressure. The details of the extraction of the rate constants from the experimental data will be included in a journal manuscript that is currently in the early stages of preparation.

We obtained a rate constant for OH($\nu$ = 4) with CO$_2$ at room temperature of (6.4 ± 0.3) × 10$^{-12}$ cm$^3$ s$^{-1}$, where the experimental uncertainty is two standard deviations. We were concerned since this value disagreed with the experimental value of Dodd et al. [7]
from 1991 of $(2.8 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$. We performed numerous experimental checks and tests and continue to obtain an experimental result that is at least a factor of two larger than the 1991 Dodd et al. value. To see if this deviation persisted to other measurements and vibrational levels we performed studies at room temperature for OH($\nu = 3$) with CO$_2$. For that vibrational level in OH we obtained a collisional removal rate constant of $(1.9 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$ which is over a factor of four slower than that obtained for $\nu = 4$. This result is in good agreement with the Dodd et al. [7] value of $(1.4 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$. Based on the agreement for the results for $\nu = 3$ and the large difference for $\nu = 4$, we conclude that the 1991 measurements of Dodd et al. [7] were complicated by collision cascade from higher vibrational levels in OH generated by their less state specific production method. The new rate constant for OH($\nu = 4$) with CO$_2$ means that for a given atmospheric composition, the emission intensity from $\nu = 4$ will be over a factor of two weaker than previously predicted using the slower rate constant.

The only previous measurement on the temperature dependence for CO$_2$ relaxation of vibrationally excited OH was performed in our laboratory several years ago for OH($\nu = 10$) [8]. We found that the rate constant was about 30\% faster at $\sim 225$ K compared to room temperature. While significant in showing that the removal rate constant may increase in low temperatures the results are not directly applicable to the vibrational levels of OH chemically produced in planetary atmospheres. In this work, we used an experimental apparatus that was capable of temperatures down to $\sim 170$ K when cooling with liquid nitrogen. For OH($\nu = 4$) with CO$_2$ at $\sim 170$ K we obtained a collisional removal rate constant of $(9.6 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$. For OH($\nu = 3$) with CO$_2$ at $\sim 170$ K we obtained a collisional removal rate constant of $(3.1 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$. Both of these rate constants show an increase of around 50\% over the temperature range. This increase is similar in magnitude to that observed in the previous results for OH($\nu = 10$) for a smaller temperature range.

The last group of experiments were to evaluate the pathways for the relaxation of OH($\nu = 4$) via a detailed study of the shape of the temporal evolution of OH($\nu = 3$). The experiments produced data with excellent signal-to-noise, however, the analysis is significantly more complicated than a single exponential fit. The analysis is still in the early stages. To synthesize the temporal evolution of OH($\nu = 3$) under our experimental conditions, we have put together a kinetic model with the best rate constants and vibrational level specific channels possible. Qualitatively, it appears that a large fraction of the OH($\nu = 4$) relaxation with CO$_2$ goes through a single quantum relaxation to produce an OH($\nu = 3$). Currently, we are performing studies under more experimental conditions and are evaluating different quantitative procedures to extract the branching ratio.

**OH($\nu = 9$) rate constant.** In the above approach if one does not photodissociate all of the ozone the reaction of hydrogen atoms with the remaining ozone generates OH in high vibrational levels. By changing the relative amounts of O$_3$ and CO$_2$ and monitoring the OH($9$) population via LIF, we obtain the relative rate constants for the two species. Using the recently measured rate constant for O$_3$ by Nizkorodov et al. [11] we obtain a CO$_2$ rate constant of $(5.6 \pm 1.4) \times 10^{-11} \text{ cm}^3 \text{s}^{-1}$. This room temperature value agrees extremely well with the previous SRI measurement of $(5.7 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{s}^{-1}$ performed via a significantly different experimental approach [2].

**Summary:** We have made new rate constant measurements for vibrationally excited OH with CO$_2$. The results significantly improve our ability to predict the intensity of OH emission in the atmosphere of Mars. Laboratory experiments addressing the pathways, other vibrational levels, and the temperature dependence will continue to improve the model.

**References:**


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