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Relaxation Processes of Vibrationally Excited H₂O in the Mesosphere and Thermosphere

Prepared by

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Prepared for

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RELAXATION PROCESSES OF VIBRATIONALLY EXCITED H₂O
IN THE MESOSPHERE AND THERMOSPHERE

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INTRODUCTION

This review is the second in a series of reports intended to update the state-of-knowledge regarding the temperature dependence of collisional energy transfer processes by potential radiators in the mesosphere and thermosphere. At the altitudes of interest (≥ 50 km), the radiating species are generally non-LTE, that is, they are not in local thermodynamic equilibrium. For this reason, the rates of spontaneous emission processes that compete with collisional relaxation processes must be included in any kinetic description of the upper atmosphere. A previous Aerospace Corporation report [TOR-0091(6078)-1, Ref. 1] described the kinetics affecting CO radiance; this report is concerned with vibrationally excited H₂O. A discussion of the non-LTE region is contained in the former.

The last major review of atmospheric kinetics that contained relaxation rates for vibrationally excited species was that of Taylor in 1974 (Ref. 2). After reviewing the literature through 1991, we concluded that there is still a need for reliable, process-specific, experimental rate data for the collisional relaxation of vibrationally excited H₂O. Recent laser-induced fluorescence experiments have improved the temperature-dependent data for the self-relaxation of H₂O and for the relaxation by O atoms. However, the temperature dependences of the relaxation pathways enabled by the dominant atmospheric species, N₂ and O₂, have not been well characterized. Ambient temperatures in the mesosphere and thermosphere typically range from 190 to 1300 K. We have compiled the available data for each relevant relaxation partner in order to obtain temperature functions. Where possible, a linear Landau-Teller form (Ref. 3) was used. Where fewer data were available, a simplified $T^{1/2}$ temperature function was estimated. The results are presented in Appendices A through C. A description of the applicability of the Landau-Teller equation is given in Ref. 1.

Since the rovibrational line strengths for H₂O have been accurately measured by high resolution spectroscopy, the vibrational band strengths are well established. The most recent version of the sum-of-lines band strengths, as compiled in the HITRAN 1991 listing (Ref. 4), have been used to calculate the spontaneous emission rates from each H₂O vibrational level. The results are described in Appendix D.

The rate constants for the energy transfer processes described here are important parameters in the calculation of radiance emitted by the upper atmosphere. The values obtained from this analysis have been incorporated into the Strategic High Altitude Radiance Code (SHARC), Version 2.0 (Ref. 5). The format for the coefficients of the rate equations listed in Table 1 has been borrowed from SHARC. The code was also used to quantify the effect of the updated rate constants on the emissions from each H₂O vibrational band. The results are summarized in Table 2 and illustrated in Figs. 2 through 4.

DATA REVIEW

Some general results and observations from our review are described in this section. Specific references, data analyses, and rate constants are presented in Appendices A through D as well as in Table 1. A vibrational energy level diagram for H₂O is given in Fig. 1, depicting the radiative processes that result in major atmospheric infrared emissions.

The V-R,T relaxation of the ν_2 (010) bending level of H₂O has been studied more than any of the other collisional relaxation processes relevant to atmospheric H₂O. However, there is still an ambiguity associated with the effect of different collision partners on the ν_2 relaxation rate. The data for the collision partners O₂, N₂, and Ar are combined in Fig. A1 (Appendix A) since these are not statistically different when the errors associated with the measurements are considered. Previous versions of SHARC contained the same rate for the relaxation of the $2\nu_2$, $3\nu_2$, $\nu_1 + \nu_2$, and $\nu_2 + \nu_3$ levels as for the ν_2 level. This is not the best approximation that can be made for all of these higher energy levels, and, therefore, we have modified these values as described in Appendix A.

The H₂O(010) level is only 39 cm⁻¹ higher in energy than the O₂(1) level. This allows for rapid V-V energy transfer from H₂O to O₂ in a process that is competitive with the V-R,T relaxation of H₂O(010). The two processes are difficult to separate experimentally, but it can be accomplished using a carefully planned laser-induced fluorescence experiment. However, the only data currently available for the V-V relaxation of the ν_2 level are acoustic data, reported with large error bars. Therefore, as shown in Fig. B1 (Appendix B), we have taken an "average" of several of these sets of data. No temperature dependence could be established over the 300 - 600 K temperature range of the data. Our rate constant, based on experimental data, is notably larger than earlier theoretical estimates made by Taylor (Ref. 2).

Previous versions of the SHARC H₂O kinetics module already contained the only experimentally measured room temperature rate constant for the V-R,T relaxation of the (001) and (100) reservoir by N₂ or O₂ (Ref. 6). Since there are no newer data available for other temperatures, we have retained this constant for those collision partners. Current model atmospheres [e.g., 1976 Standard, (Ref. 7)] generally indicate that the number density of H₂O decreases to an insignificant amount at altitudes where O(³P) could be a potential collision partner. Since laser induced fluorescence measurements near room temperature are available for the rate constant of V-T energy transfer from H₂O(001) or (100) to O(³P), these data are briefly described in Appendix C for use with any non-typical model atmospheres that may have an unusually high H₂O content at high altitudes.

Table 1. Rate Coefficients for Relaxation of Vibrationally Excited H₂O
 $[k_i = A_i T^{\beta_i} \exp(-C_i/T - 333 - E_i/T)]$

REACTIONS	PREVIOUS COEFFICIENTS (a,b)				REVISED COEFFICIENTS(c)			
					A _i	β _i	C _i	*E _i
M + H ₂ O(010) = M + H ₂ O(000) N ₂ /1.0/ O ₂ /1.0/	5.37E-10	0.0	70.0	0.0	1.13E-10	0.0	52.5	0.0
M + H ₂ O(100) = M + H ₂ O(020) N ₂ /1.0/ O ₂ /0.7/ O(3P)/8.7/	4.60E-13	0.0	0.0	0.0	4.60E-13	0.0	0.0	0.0
M + H ₂ O(001) = M + H ₂ O(020) N ₂ /1.0/ O ₂ /0.7/ O(3P)/8.7/	4.60E-13	0.0	0.0	0.0	4.60E-13	0.0	0.0	0.0
M + H ₂ O(001) = M + H ₂ O(100) N ₂ /1.0/ O ₂ /1.0/	-----	-----	-----	-----	1.20E-11	0.5	0.0	0.0
M + H ₂ O(020) = M + H ₂ O(010) N ₂ /1.0/ O ₂ /1.0/	5.37E-10	0.0	70.0	0.0	2.26E-10	0.0	52.5	0.0
M + H ₂ O(030) = M + H ₂ O(020) N ₂ /1.0/ O ₂ /1.0/	5.37E-10	0.0	70.0	0.0	3.39E-10	0.0	52.5	0.0
M + H ₂ O(110) = M + H ₂ O(100) N ₂ /1.0/ O ₂ /1.0/	5.37E-10	0.0	70.0	0.0	1.13E-10	0.0	52.5	0.0
M + H ₂ O(011) = M + H ₂ O(001) N ₂ /1.0/ O ₂ /1.0/	5.37E-10	0.0	70.0	0.0	1.13E-10	0.0	52.5	0.0
M + H ₂ O(110) = M + H ₂ O(030) N ₂ /1.0/ O ₂ /0.7/	4.60E-13	0.0	0.0	0.0	4.60E-13	0.0	0.0	0.0
M + H ₂ O(011) = M + H ₂ O(030) N ₂ /1.0/ O ₂ /0.7/	4.60E-13	0.0	0.0	0.0	4.60E-13	0.0	0.0	0.0
O ₂ (0) + H ₂ O(010) - O ₂ (1) + H ₂ O(000) O ₂ (1) + H ₂ O(000) - O ₂ (0) + H ₂ O(010) O ₂ (0) + H ₂ O(020) - O ₂ (1) + H ₂ O(010) O ₂ (1) + H ₂ O(010) - O ₂ (0) + H ₂ O(020) O ₂ (0) + H ₂ O(030) - O ₂ (1) + H ₂ O(020) O ₂ (1) + H ₂ O(020) - O ₂ (0) + H ₂ O(030) O ₂ (0) + H ₂ O(110) - O ₂ (1) + H ₂ O(100) O ₂ (1) + H ₂ O(100) - O ₂ (0) + H ₂ O(110) O ₂ (0) + H ₂ O(011) - O ₂ (1) + H ₂ O(001) O ₂ (1) + H ₂ O(001) - O ₂ (0) + H ₂ O(011)	1.00E-12 1.00E-12 1.00E-12 1.00E-12 1.00E-12 1.00E-12 1.00E-12 1.00E-12 1.00E-12	0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	0.0 55.2 0.0 0.7 0.0 -59.3 0.0 31.0 0.0 27.3	2.9E-12 2.9E-12 5.8E-12 5.8E-12 8.7E-12 8.7E-12 2.9E-12 2.9E-12 2.9E-12 2.9E-12	0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	0.0 55.8 0.0 1.3 58.8 0.0 0.0 31.6 0.0 27.8

Table 1. Rate Coefficients for Relaxation of Vibrationally Excited H₂O (cont.)

REACTIONS	PREVIOUS COEFFICIENTS (a,b)				REVISED COEFFICIENTS(c)			
	A _i	β _i	C _i	*E _i	A _i	β _i	C _i	*E _i
H ₂ O(010) - H ₂ O(000) + HV	18.350.0	0.0	0.0	0.0	20.33	0	0	0
H ₂ O(020) - H ₂ O(000) + HV	0.454	0.0	0.0	0.0	0.567	0	0	0
H ₂ O(100) - H ₂ O(000) + HV	3.37	0.0	0.0	0.0	5.00	0	0	0
H ₂ O(001) - H ₂ O(000) + HV	78.40	0.0	0.0	0.0	76.58	0	0	0
H ₂ O(030) - H ₂ O(000) + HV	0.003	0.0	0.0	0.0	0.0065	0	0	0
H ₂ O(110) - H ₂ O(000) + HV	0.349	0.0	0.0	0.0	0.7680	0	0	0
H ₂ O(011) - H ₂ O(000) + HV	17.22	0.0	0.0	0.0	17.23	0	0	0
H ₂ O(020) - H ₂ O(010) + HV	33.74	0.0	0.0	0.0	41.29	0	0	0
H ₂ O(100) - H ₂ O(010) + HV	0.612	0.0	0.0	0.0	1.36	0	0	0
H ₂ O(001) - H ₂ O(010) + HV	3.70	0.0	0.0	0.0	2.15	0	0	0
H ₂ O(030) - H ₂ O(010) + HV	1.11	0.0	0.0	0.0	1.21	0	0	0
H ₂ O(110) - H ₂ O(010) + HV	4.17	0.0	0.0	0.0	4.53	0	0	0
H ₂ O(011) - H ₂ O(010) + HV	65.98	0.0	0.0	0.0	71.49	0	0	0
H ₂ O(030) - H ₂ O(020) + HV	36.87	0.0	0.0	0.0	40.06	0	0	0
H ₂ O(000) + HV - H ₂ O(010)	0.0	0.0	0.0	0.0	-----	--	--	--
H ₂ O(000) + HV - H ₂ O(020)	0.0	0.0	0.0	0.0	-----	--	--	--
H ₂ O(000) + HV - H ₂ O(100)	0.0	0.0	0.0	0.0	-----	--	--	--
H ₂ O(000) + HV - H ₂ O(001)	0.0	0.0	0.0	0.0	-----	--	--	--
H ₂ O(000) + HV - H ₂ O(030)	0.0	0.0	0.0	0.0	-----	--	--	--
H ₂ O(000) + HV - H ₂ O(110)	0.0	0.0	0.0	0.0	-----	--	--	--
H ₂ O(000) + HV - H ₂ O(011)	0.0	0.0	0.0	0.0	-----	--	--	--
H ₂ O(010) + HV - H ₂ O(020)	0.0	0.0	0.0	0.0	-----	--	--	--
H ₂ O(010) + HV - H ₂ O(100)	0.0	0.0	0.0	0.0	-----	--	--	--
H ₂ O(010) + HV - H ₂ O(001)	0.0	0.0	0.0	0.0	-----	--	--	--
H ₂ O(010) + HV - H ₂ O(030)	0.0	0.0	0.0	0.0	-----	--	--	--
H ₂ O(010) + HV - H ₂ O(110)	0.0	0.0	0.0	0.0	-----	--	--	--
H ₂ O(010) + HV - H ₂ O(011)	0.0	0.0	0.0	0.0	-----	--	--	--
H ₂ O(020) + HV - H ₂ O(030)	0.0	0.0	0.0	0.0	-----	--	--	--

a) R. L. Taylor, Can. J. Chem., 52, 1381 (1974) and/or SHARC versions < 2.0.

b) This review.

* The E_i terms (i.e., the energy differences between levels) are not listed here for the V-T processes because these are obtained from the H₂OSTAT.DAT file in SHARC 2.0.

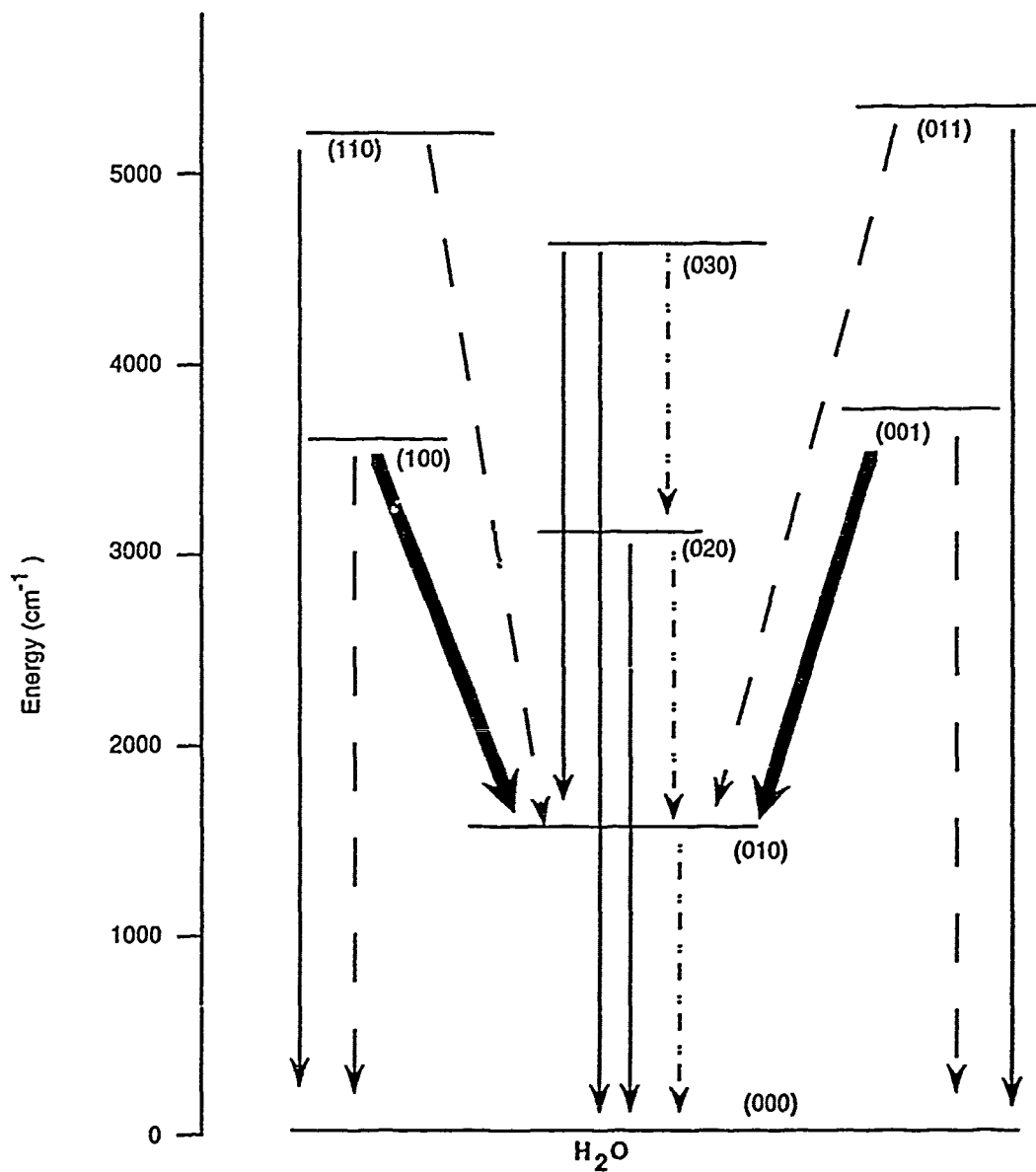


Figure 1. Vibrational bands contributing to H₂O infrared emissions in the upper atmosphere. Prominent atmospheric features occur near 6.4 mm - - - - -, 4.7 μ m **————** and 2.7 μ m ————.

Einstein A coefficients for all the relevant radiative relaxation processes of vibrationally excited H₂O have been calculated using the 1991 HITRAN sum-of-lines band strengths, S_{ul} . Changes to certain H₂O rovibrational lines have been made to the HITRAN listing since the 1986 version (Ref. 8). Some of the emission rates we calculated were approximately twice as high as those previously used in SHARC. Although the line list for H₂O has been improved since 1986, the changes are not large enough to cause such significant differences in the band strengths. Rates calculated from the first coefficients of the transition dipole moments reported in the literature rather than from the band strengths may have been the source of the discrepancy. Dipole moment calculations are not straightforward for many H₂O transitions since Fermi and Coriolis interactions occur between closely spaced vibrational levels. In most cases, the full functional form of the transition dipole necessary for calculating a band strength is not explicitly given by the authors who reported H₂O line strengths. We have attempted to standardize the emission rates using the S_{ul} values so that discrepancies in the application of the theoretical parameters for the vibrational and rovibrational interactions can be avoided.

SHARC RADIANCE OUTPUT

The updates described above have been incorporated into a new input file for the ambient H₂O kinetics module in SHARC. These rates are given in Table 1 in the format currently used in SHARC (Version 2.0, Aerospace Corporation preliminary copy). A test calculation using a SHARC model atmosphere profile was performed. A subarctic daytime model atmosphere was used since the lower altitude concentrations of H₂O are larger than those in the Standard 1976 models. The results of the test are presented in Table 2 and Figs. 2 through 4. A limb view at 64 km tangent height was used with an arbitrary latitude and longitude of (0,0) chosen for illustrative purposes only. Ideally a region-specific equatorial model with large column densities of H₂O would have been preferred.

The radiances calculated by SHARC using the new kinetics scheme are generally smaller than or equal to those calculated with the old rates. The band radiances for each H₂O vibrational transition and the ratios (old:new) are listed in Table 2. The decreased emissions are a result of increasing the collisional relaxation rates of the upper vibrational levels, or effectively quenching the excited molecules before they can radiate. This effect apparently dominates over the increases made to some of the spontaneous emission rates. Transitions originating in the 3v₂ level (centered at 4667 cm⁻¹, 3072 cm⁻¹, and 1515 cm⁻¹) are a factor of 12.6 times weaker after changing the kinetics. Similarly, transitions originating in the 2v₂ level are 5.2 times weaker. The overall effect on the radiance in particular cm⁻¹ regions is illustrated in Figs. 2 through 4. Our calculations indicate that the (020) - (000) band centered at 3150 cm⁻¹ will be narrower due to less intense radiance on the high frequency side than previously predicted. This effect is evident in Fig. 4. Such changes to the more intense H₂O infrared bands have important consequences for atmospheric sensor development.

Table 2. Band Radiance Comparison

Transition	Frequency	Band Radiance (W/sr·cm ²)		Radiance Ratio Old:New
		Old Kinetics	New Kinetics	
(010)-(000)	1594.750	0.37277e-6	0.35466e-6	1.05
(020)-(000)	3151.630	0.11184e-8	0.21412e-9	5.22
(100)-(000)	3657.053	0.87024e-9	0.47780e-9	1.82
(001)-(000)	3755.930	0.35921e-7	0.36124e-7	0.994
(030)-(000)	4666.793	0.11070e-11	0.87792e-13	12.6
(110)-(000)	5234.977	0.63862e-11	0.24911e-11	2.56
(011)-(000)	5331.269	0.20763e-8	0.12812e-8	1.62
(020)-(010)	1556.880	0.39202e-7	0.75069e-8	5.22
(100)-(010)	2062.303	0.13254e-9	0.73330e-10	1.81
(001)-(010)	2161.180	0.16949e-8	0.16950e-8	1.00
(030)-(010)	3072.043	0.17710e-9	0.14089e-10	12.6
(110)-(010)	3640.227	0.39018e-10	0.15291e-10	2.55
(011)-(010)	3736.519	0.82490e-8	0.50967e-8	1.62
(030)-(020)	1515.163	0.32288e-8	0.25724e-9	12.6
Pure Rotational Lines		0.99151e-10	0.99151e-10	1.0
Total Overlap Corrected Bandpass Radiance		0.46488e-6	0.40686e-6	1.14

Model Atmosphere: DAYSUBAR.DAT

Limb View, 64 km Tangent

Lat. 0°, Long. 0°

Solar Zenith Angle 0°

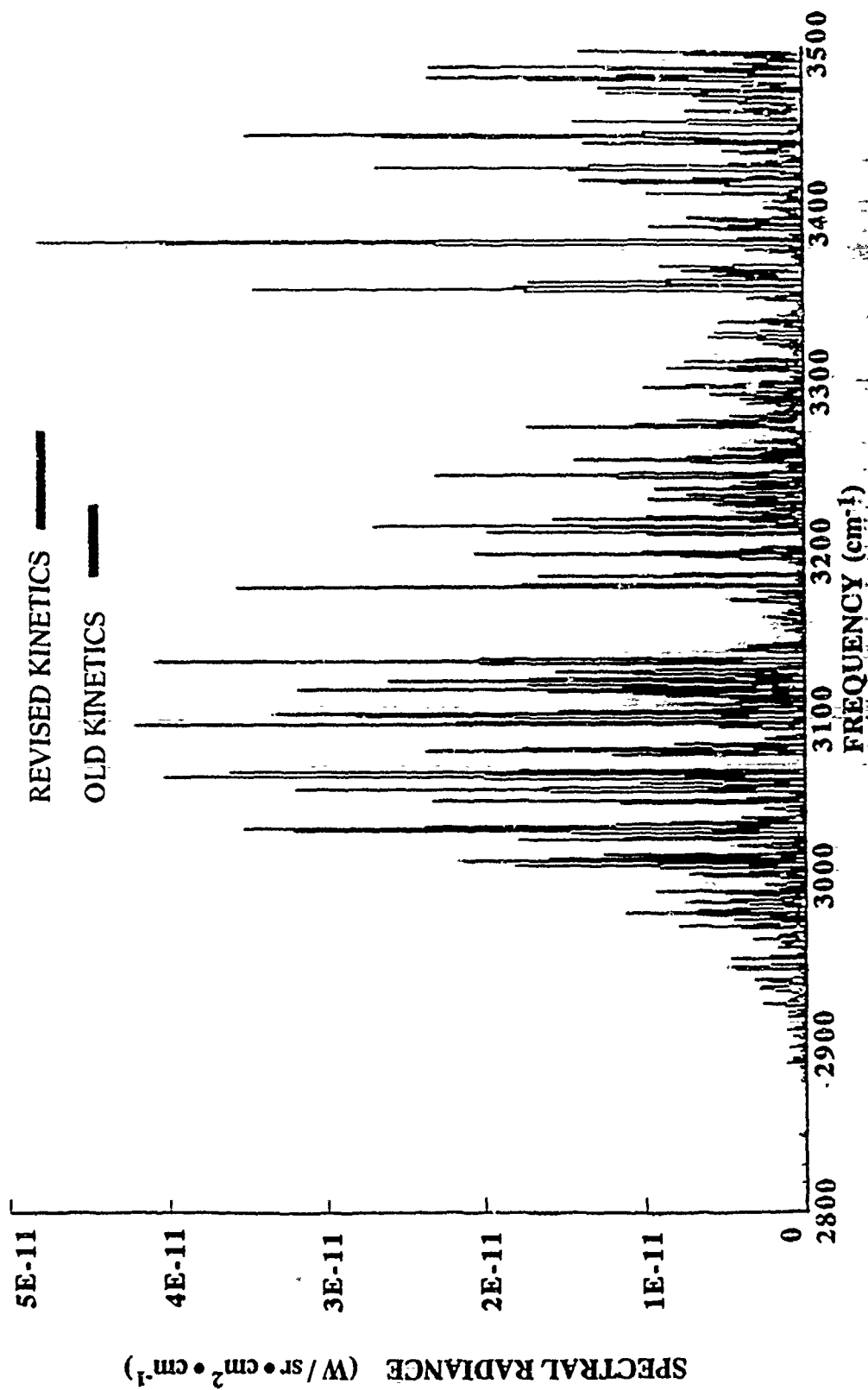


Figure 2. SHARC 2.0 limb calculation of H₂O infrared radiance using old kinetics (Ref. 2) and revised constants (this review). Main feature in this region is the (020) - (000) rovibrational band.

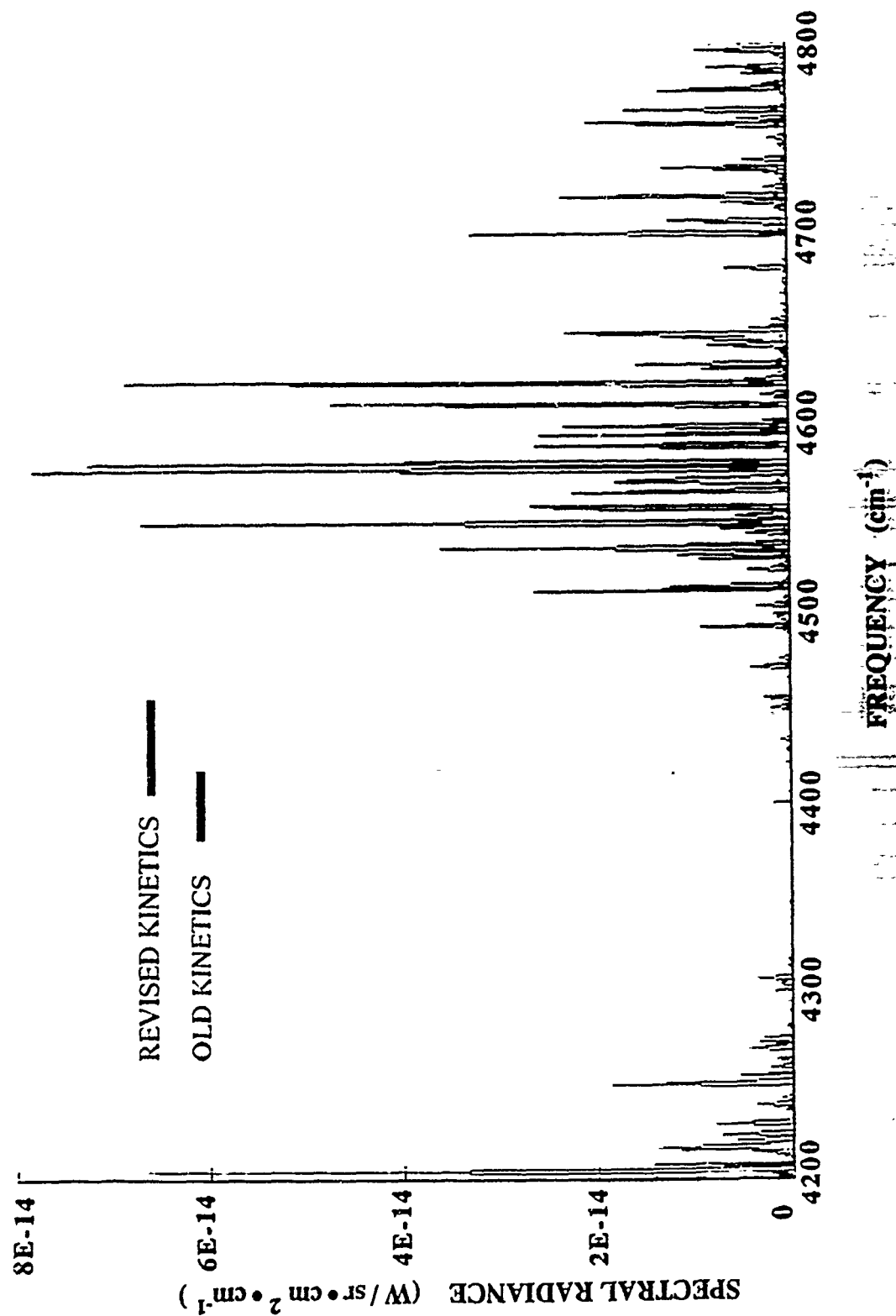


Figure 3. SHARC 2.0 limb calculation of H₂O infrared radiance. Main feature in this region is the (030) - (000) rovibrational band.

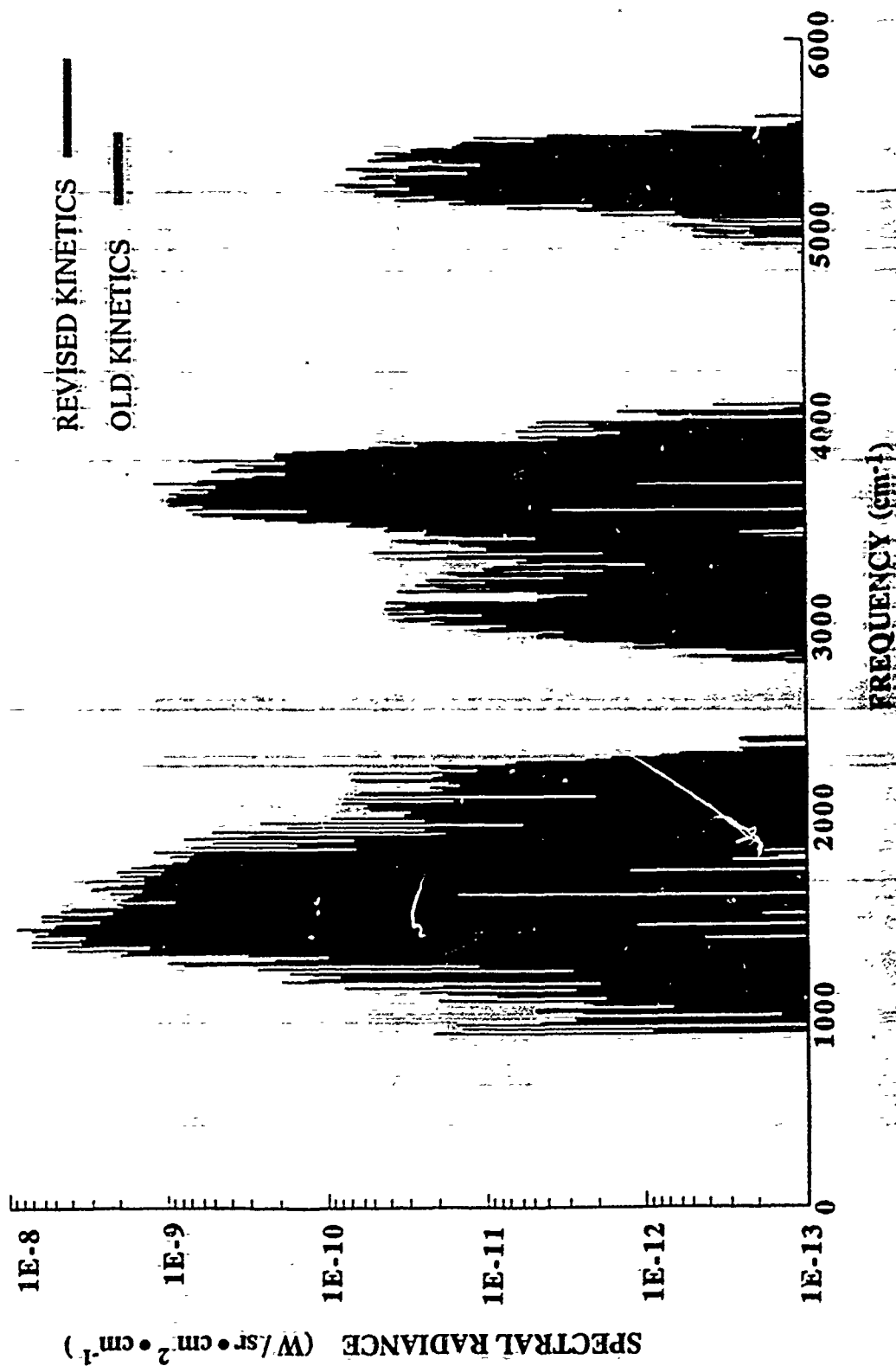


Figure 4. SHARC 2.0 limb calculation of H₂O infrared radiance. Effect of revising the relaxation rate constants is illustrated.

SUMMARY

While there is still room for improvement in experimental measurements of the $\text{H}_2\text{O}(010)$ vibrational relaxation processes, some progress has been made since 1974 when several of the rates reported by Taylor were based on theoretical inferences.

Essentially all of the individual collisional relaxation processes need further experimental investigation as a function of temperature. Laser-induced fluorescence techniques would be particularly useful in verifying previous acoustic measurements as well as accumulating data in the temperature region below the shock-tube limit and above room temperature. The V-V and V-T contributions to the overall relaxation of the ν_2 bending level by O_2 still need to be quantified.

Since the vibrational line strengths for the H_2O emission bands used in radiance codes such as SHARC have been accurately measured by high-resolution infrared spectroscopy, the spontaneous emission coefficients are well established.

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APPENDIX A

V-R,T RELAXATION OF H₂O ν_2 BEND AND ν_2 COMBINATION LEVELS

a) Relaxation of ν_2 by O₂ and N₂

The two predominant gases in the mesosphere that can act as collision partners for vibrationally excited H₂O are O₂ and N₂. The non-radiative relaxation from the ν_2 level can be expressed as



The H₂O kinetics module in earlier versions of SHARC contained the following temperature dependence for the V-T (or V-R,T) relaxation of the ν_2 level of H₂O:

$$k_1^{\text{old}} \text{ forward} = 5.37\text{e-}10 \exp(-69.918/T.333) \quad 200 - 400 \text{ K} \quad (\text{A2})$$

This rate equation is from the 1974 review article by Taylor (Ref. A1) and has a quoted uncertainty of an order of magnitude. The original research on which this Arrhenius equation is based was that of Monk (Ref. A2), who only measured rates at 295 K, using a sound absorption technique. It appears that Taylor derived an average rate constant for the relaxation of H₂O(010) by N₂ + O₂ from two room temperature values (which differ by a factor of 23) and then applied a theoretical temperature dependence. That O₂ and N₂ are equally efficient partners is a reasonable assumption for the V-R,T relaxation of H₂O(010). However, Monk's data are too widespread to support this assumption (see Fig. A1). Another problem lies in the relative magnitudes of Monk's data. It is inherently difficult to separate the near-resonant V-V energy transfer from H₂O(010) to O₂(100) from the V-T relaxation of H₂O(010) by O₂. However, if the V-T contribution to the overall relaxation process is approximately the same as the V-T rate with N₂, this fraction could be subtracted from the overall O₂ rate. The major inconsistency in Monk's data is the fact that the V-T rate with O₂ is reported to be 23 times slower than that with N₂. We would expect the former to be larger by a small amount.

In all of the low temperature studies (295 - 600 K) reported in the literature (Refs. A2, A3 and A4), the acoustic techniques used to derive relaxation rate constants for Reaction A1 depend on the validity of approximations made for several concurrent energy transfer processes in a mixture of gases. The experiments were generally designed to study the dependence of Napier frequencies (frequency of maximum sound absorption per meter) as a function of O₂ and H₂O concentrations in gaseous mixtures such as air. While only a few rates were actually

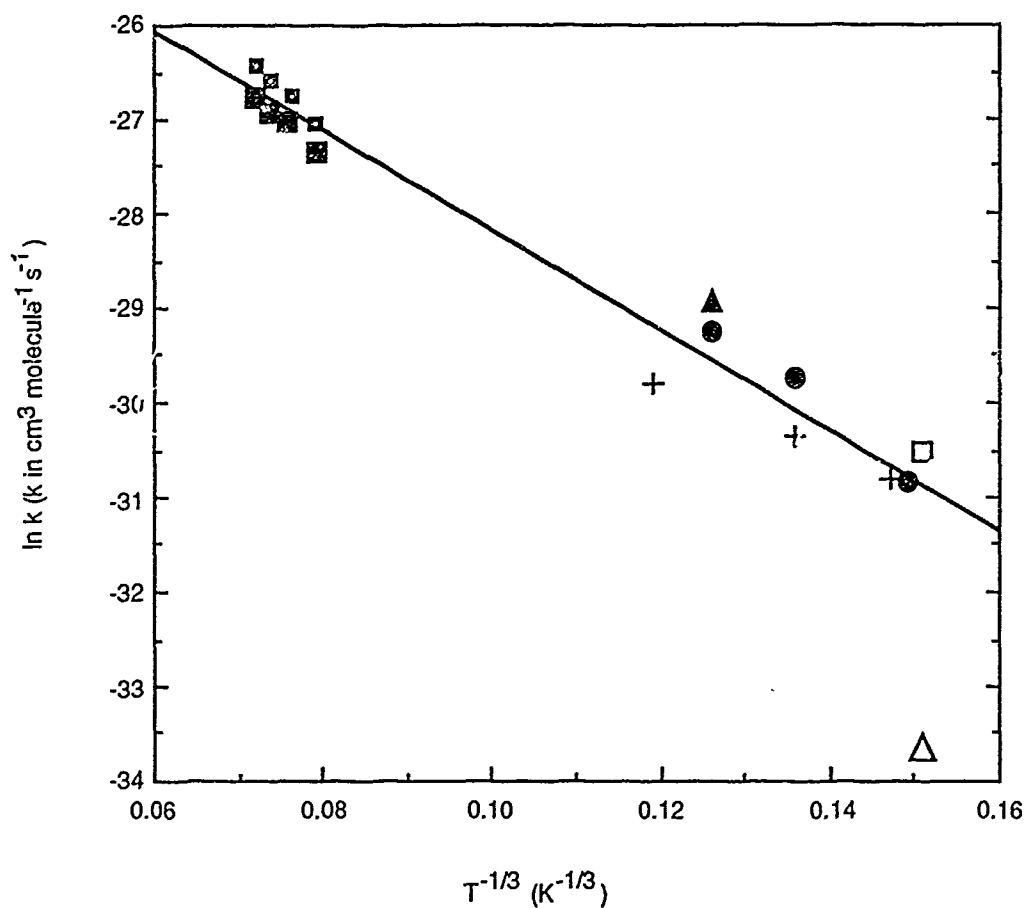


Figure A1. v -R,T relaxation of $\text{H}_2\text{O}(010)$. Data used in present fit: Kung and Center (Ref. A6), N_2 ■, Ar ■; Bass et. al. (Ref. A3), O_2 ●; Keeton and Bass (Ref. A4), N_2 or Ar ▲; Bass and Shields (Ref. A5), O_2 +. Data used by Taylor (Ref. A1) and not included in present fit: Monk (Ref. A2), O_2 △, N_2 □.

measured, five to seven reversible energy transfer processes were needed to stoichiometrically balance the Napier problem and to fit the experimental frequencies to a concentration curve. Examination of the procedures used by several investigators reveals that those employed by Bass, Keeton, and Williams (Ref. A3) are more self-consistent than those of earlier investigators (Monk, Ref. A2). However, the conclusions drawn by Bass et al. are questionable because they erroneously plotted data from other sources (e.g., Kung and Center, Ref. A6) as well as from their own tables.

Without going into the details of the various approximations made by different investigators, we report here the most consistent of the results from the acoustic experiments (Ref. A3, A4 and A5) for 400, 500 and 600 K. However, the individual data points from these references are not necessarily experimentally unique. The author Bass was involved in each of these studies and has incorporated the actual measurements into an iterative fitting procedure to compute the temperature dependence given in Ref. A3. We have combined the accumulated acoustic data with high temperature shock wave data for the collisional relaxation rates of H₂O (010). The latter data were taken from the original paper by Kung and Center (Ref. A6). A statistical energy distribution using the heat capacity, C_v , and the vibrational temperature, θ_T , was applied to the experimentally measured rates to correct for bulk heating inherent in the shock tube method. The authors estimate that their rate constants are accurate to within a factor of 2.

In summary, it is recommended that the functional form of the temperature dependence for the H₂O (010) V-T relaxation be updated to reflect the experimental shock tube data and the consensus of the acoustic data. In our analysis, we assumed that the V-T transfer efficiencies of N₂ and O₂ are approximately equal. We used the data for the relaxation of H₂O by Ar as well as by O₂ and N₂ since the molecular mass of O₂ lies between that of Ar and N₂. The temperature dependence obtained from fitting the combined data to a Landau-Teller function (see Fig. A1) is

$$k_1^{\text{new}} = 1.13 \times 10^{-10} \exp(-52.5/T^{.333}) \quad 295 - 2000 \text{ K} \quad (\text{A3})$$

The $T^{-.333}$ coefficient was obtained from the slope of Fig. A1 while the pre-exponential factor is equal to the exponential of the ordinate intercept. At 300 K, the rate constant from Taylor's function is $1.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ compared with our new value of $4.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. However, this factor-of-3 difference decreases as the temperature increases from room temperature up to ~1500 K.

The rate for the corresponding reverse process (i.e., collisional excitation of H₂O in the v_2 mode) includes the energy difference [$E_1 = \Delta E (\text{cm}^{-1} \times 1.44 \text{ K/cm}^{-1})$] between ground state H₂O and H₂O (010). That is,

$$k_1^{\text{new}}_{\text{reverse}} = 1.13 \times 10^{-10} \exp(-52.5/T^{.333} - 2296.4/T) \quad (\text{A4})$$

where the band ν_2 band center frequency is 1594.74 cm^{-1} . Since the SHARC 2.0 code accesses the H₂O States file for the E_1 variable for the V-R,T relaxation processes, these are not listed in Table 1. The energies of the vibrational bands can also be found in the 1991 HITRAN (Ref. A7) line list.

Since the low temperature rate constants for the relaxation of H₂O by N₂ and O₂ contain so much uncertainty (~ order of magnitude) it would be worthwhile to measure the rates over the 180 -1000 K temperature range using laser-induced fluorescence (LIF). The bulk methods previously employed for the study of ν_2 lack the capability of selective excitation of a particular level. LIF has been used successfully to study other collision partners and other vibrationally excited levels of H₂O (e.g., Refs. A8, A9).

b) V-R,T Relaxation of the $2\nu_2$ and $3\nu_2$ Levels

In previous versions of SHARC, k_1 for the V-R,T relaxation of the H₂O (010) level by N₂ and O₂ was also used for the hot emission bands, $3\nu_2 - 2\nu_2$ and $2\nu_2 - \nu_2$. Using the harmonic oscillator approximation, the rates for these V-T relaxation mechanisms of H₂O would be 3 and 2 times greater, respectively, than that for the $\nu_2 - 0$ fundamental process. The revised rate expressions for collisional relaxation with equal efficiency by M = O₂ or N₂ are

$$\begin{aligned} \text{M} + \text{H}_2\text{O}(020) &= \text{M} + \text{H}_2\text{O}(010); \\ k_2^{\text{new}}_{\text{forward}} &= 2.26 \times 10^{-10} \exp(-52.5/T^{.333}) \text{ and} \end{aligned} \quad (\text{A5})$$

$$k_2^{\text{new}}_{\text{reverse}} = 2.26 \times 10^{-10} \exp(-52.5/T^{.333} - 2241.9/T) \quad (\text{A6})$$

and

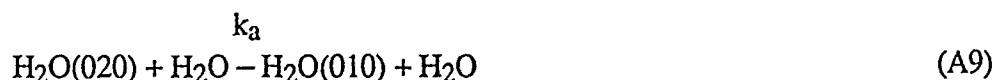
$$\begin{aligned} \text{M} + \text{H}_2\text{O}(030) &= \text{M} + \text{H}_2\text{O}(020); \\ k_3^{\text{new}}_{\text{forward}} &= 3.39 \times 10^{-10} \exp(-52.5/T^{.333}) \text{ and} \end{aligned} \quad (\text{A7})$$

$$k_3^{\text{new}}_{\text{reverse}} = 3.39 \times 10^{-10} \exp(-52.5/T^{.333} - 2181.8/T) \quad (\text{A8})$$

The band center frequencies of 1594.74 cm^{-1} , 3151.63 cm^{-1} and 4666.8 cm^{-1} for the ν_2 , $2\nu_2$, and $3\nu_2$ levels, respectively, were used to obtain the energy difference terms for the reverse processes.

Since the rate coefficients for the overtone transitions from $3\nu_2$ and $2\nu_2$ to the ground state are assumed to be much smaller than those for transfer of a single quantum of vibrational energy, they are not included in our overall kinetics scheme.

Experimental evidence for the validity of using the harmonic oscillator approximation for the case of H₂O vibrational relaxation has been found in laser-induced fluorescence studies (Ref. A8 and A10). This is worth mentioning here because it might be expected that strong dipole interactions or hydrogen bonding by H₂O would result in non-ideal gaseous mixtures. The two processes involving H₂O self-relaxation,



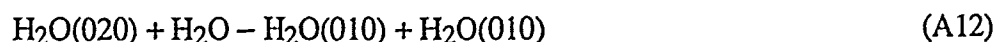
and



were investigated experimentally. It was found that the rate of the relaxation from $2\nu_2 - \nu_2$ was greater than that from $\nu_2 - 0$ and potentially twice as fast. The following limits were assigned,

$$2k_a \geq k_b > k_a \quad (\text{A11})$$

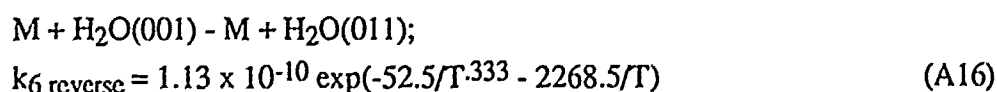
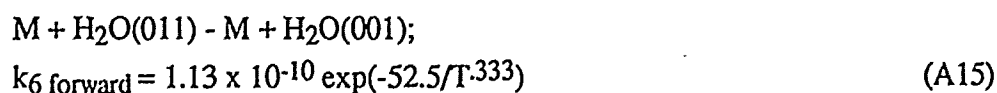
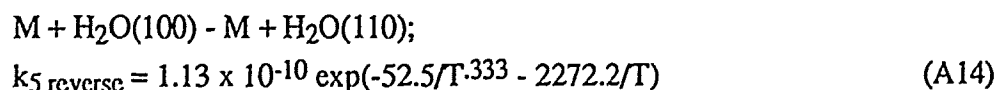
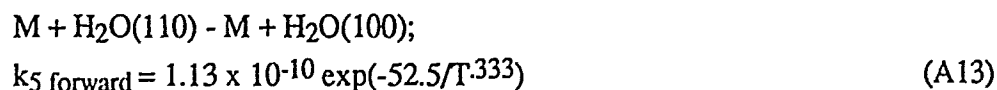
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was found to be insignificant in comparison. In Ref. A8, the relaxation of H₂O by rare gases was not studied in as much detail as the self-relaxation case.

c) V-R,T Relaxation of ν_2 Combination Levels ($\nu_1 + \nu_2$, $\nu_2 + \nu_3$)

For the SHARC reactions involving relaxation of one quantum of ν_2 from a combination level, the rate used for relaxation of the ν_2 level (k_1) can be used. The energy transferred is comparable in these three cases ($1574 - 1593 \text{ cm}^{-1}$), and, therefore, the increase in rate as a function of temperature should also be similar.



The energies of the $\nu_1 + \nu_2$, ν_1 , $\nu_2 + \nu_3$, and ν_3 band centers are 5235.0 cm^{-1} , 3657.08 cm^{-1} , 5331.279 cm^{-1} , and 3755.92 cm^{-1} , respectively. The band center frequencies were used to obtain the energy level discrepancies for the reverse processes.

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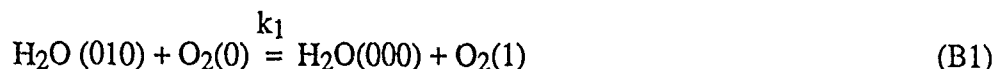
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APPENDIX B

V-V RELAXATION OF H₂O BY O₂

a) Relaxation of the H₂O(010) Level

The O₂(1) level is only 38 cm⁻¹ lower in energy than the H₂O(010) level. This coincidence facilitates rapid resonant V-V energy transfer from H₂O(010) to O₂. That is,



This process competes with the relaxation of H₂O(010) via the V-(R),T channels described in Appendix A. There have been no experiments to date designed to specifically separate the V-V and V-R,T contributions from the total relaxation rate of the 2v₂ H₂O level by O₂. This would be a difficult task even using laser-induced fluorescence data since both amplitude subtraction as well as decay time separation is involved. Alternatively, if the assumption that H₂O(010) relaxation by N₂ via a purely V-R,T mechanism is approximately equal to the V-R,T component of the relaxation by O₂, a reasonable approximation to the latter rate could be made. The V-R,T contribution could then be subtracted from the overall O₂ rate, leaving the V-V rate. This assumption is valid because there are no resonant V-V channels available with N₂.

For many kinetic applications, the rate determining step is the most important process. Since relaxation via a V-V energy transfer is often much faster than relaxation through a V-T channel, the faster rate is usually neglected. However, in modeling systems with high vibrational temperatures, such as H₂O in the thermosphere, the V-V fundamental relaxation rate of H₂O(010) is used to infer rates for four other reversible relaxation processes from higher vibrational levels of H₂O by O₂. Each process involves the transfer of one quantum of v₂ energy. Overall, the five processes involved could significantly affect the radiance from the H₂O bands. For this reason, it would be preferable to characterize the V-V and V-T rate constants explicitly.

In Taylor's 1974 review (Ref. B1), a temperature-independent rate of 1.0 x 10⁻¹² cm³ molecule⁻¹ s⁻¹ was assumed for the forward rate of the reversible process, B1. This rate constant was based on a limited amount of theoretical information (Ref. B2).

Using the Tuesday-Boudart hypothesis (Ref. B3) for the five reversible energy transfer processes possible in a heated mixture of H₂O and O₂, Bass and Shields (Ref. 3, 1974), and later Bass, Keeton and Williams (Ref. 4, 1976) found rate constants for k_{1 reverse} at 400, 500 and 600 K. These were not direct measurements, but rather the results of an iterative procedure using experimental rates for three of the five processes in the mixture. The experimental values were from acoustic measurements. The data from each of the Bass references is plotted

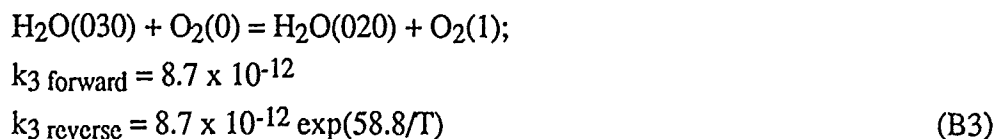
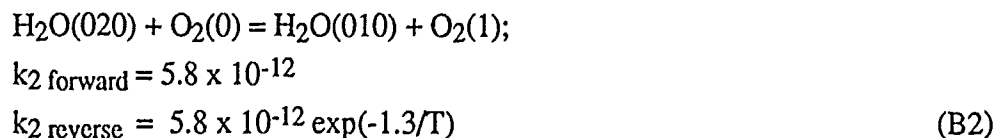
in Fig. B1. The figure also contains a room-temperature theoretical prediction by Jones et al. (Ref. B5). Since several of the reported rates were for $k_{1 \text{ reverse}}$, they were converted to the corresponding forward rate constants using the $-E_1/T$ term (where $E_1 = 55.2$) before being plotted.

There is no temperature dependence evident over the very limited temperature range covered by the data in Fig. B1. The errors associated with the data vary from conservative estimates of 50% to an order of magnitude; therefore, the data did not warrant a full Landau-Teller fitting procedure. All of the data lie above or equal to the temperature-independent rate constant proposed by Taylor (Ref. B1) and used in previous versions of SHARC. Taylor's estimated constant is really a lower limit over the $\sim 200 - 400$ K range. The average of 9 data points, including one for Taylor's estimate, yields a rate constant of $k_{1 \text{ forward}} = 2.8 \pm .4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. As the temperature increases, the reverse process, relaxation of $\text{O}_2(1)$ by H_2O , will become slightly more significant. The energy discrepancy for the reverse process is 38.3 cm^{-1} so $k_{1 \text{ reverse}} = 2.9 \times 10^{-12} \exp(-55.8/T)$. However, apart from this shift in the population distribution between the $\text{H}_2\text{O}(010)$ and $\text{O}_2(1)$ states, a relatively small temperature dependence is expected for the rates of such resonant energy transfer processes.

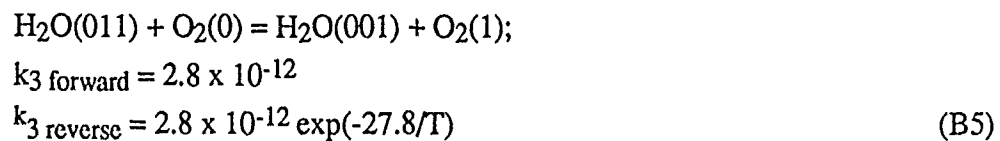
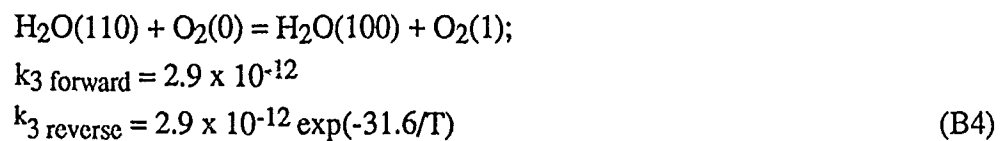
b) V-V Relaxation from Higher Vibrational Levels

In previous versions of SHARC, the same lower limit to the rate of $\text{H}_2\text{O}(010)$ V-V relaxation by O_2 was used for all the V-V relaxation processes of upper vibrational levels containing a ν_2 mode.

Applying the harmonic oscillator approximation to the rate of energy transfer from H_2O to O_2 by the V-V mechanism, we can multiply the rate for the $\text{H}_2\text{O}(\nu_2 - 0)$ process by factors of two and three for the $(2\nu_2 - \nu_2)$ and $(3\nu_2 - 2\nu_2)$ transitions, respectively. In units of $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, the assigned rates are as follows:



Two other near-resonant V-V energy transfer processes from higher combination levels of H_2O to the $\text{O}_2(1)$ level are possible:



The rate constants for Reactions B4 and B5 are approximately equal to k_1 since the v_2 quantum number of the upper H_2O levels is one, and since only one quantum of energy from the v_2 mode is transferred.

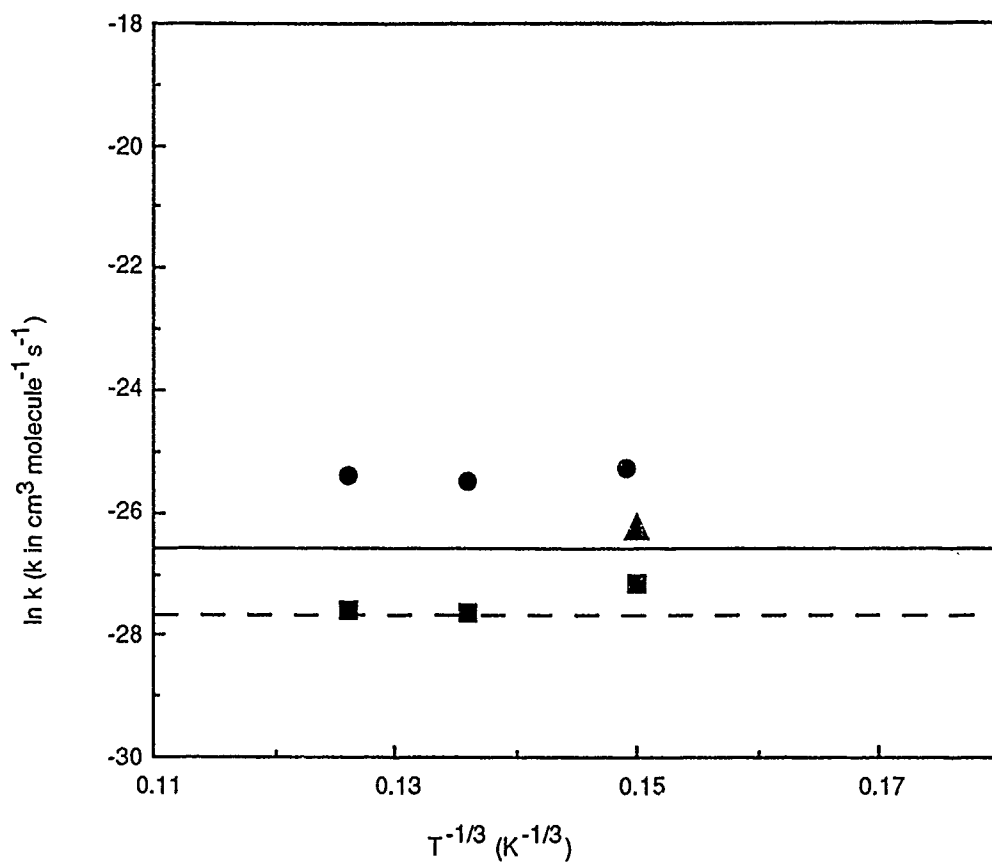


Figure B1. V-V relaxation of $H_2O(010)$ by O_2 . Data from Bass, et. al. (Ref. B4), ●; Jones et. al. (Ref. B5), ▲; Bass and Shields (Ref. B3), ■. Average from this analysis —. Constant from Taylor (Ref. B1), ---.

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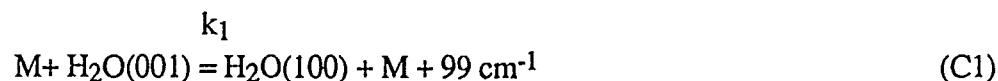
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APPENDIX C

V-R,T RELAXATION OF THE ν_1, ν_3 STRETCHING RESERVOIR AND COMBINATION LEVELS

a) $\text{H}_2\text{O}(100), (001)$ Relaxation by O_2, N_2

The energy difference between the band centers of the ν_1 and ν_3 stretching levels of H_2O is 99 cm^{-1} . Intramolecular energy transfer between these levels is facilitated by collision with a third body,

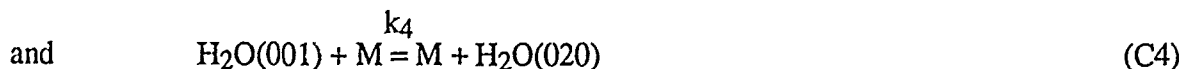


Single collisions with a third body are probably enough to cause this intramolecular energy transfer in H_2O to occur at room temperature. The rapid equilibration between the (001) and (100) levels has been observed by Finzi et al. (Ref. C1). We estimate that the rate constant k_1 is gas kinetic at room temperature. Based on the collision cross-sections of H_2O and N_2 , the temperature dependence is estimated to be

$$k_1 = 1.2 \times 10^{-11} T^{1/2} \quad (\text{C2})$$

The bidirectional interconversion, reaction C1, is rapid compared to that of energy transfer processes to lower vibrational levels. Furthermore, V-T energy transfer from either the ν_1 or ν_3 level to the $2\nu_2$ level (505 cm^{-1} or 604 cm^{-1} lower in energy, respectively) occurs at essentially the same rate.

One rate constant is assigned to both



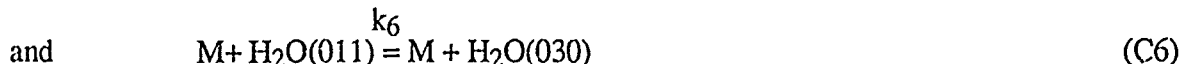
Finzi et al. (Ref. B1) measured laser-induced fluorescence from the (ν_1, ν_3) reservoir to obtain a room temperature relaxation rate constant to the $\text{H}_2\text{O}(020)$ level. The experimentally measured quantity is actually a weighted average of k_3 and k_4 . Their values for k_3 forward were $4.6 \pm 1.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $\text{M} = \text{N}_2$ and $3.3 \pm 1.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $\text{M} = \text{O}_2$. Efficiency coefficients of 1.0 and 0.7 are used to differentiate between the N_2 and O_2 rate constants in Table 1 and in SHARC. Unfortunately no information regarding the tempera-

ture dependence of these rate constants is yet available. Kung and Center (Ref. C2), who investigated other H₂O vibrational levels in their shock tube experiments, mention an overall rate for the relaxation at the stretch reservoir, but they included processes whereby 2v₂ and v₂ were relaxed to the ground state. They made the assumption that the latter step was rate determining; this was later disproven in the work of Finzi et al. Earlier rate constants suggested by Taylor (Ref. C3) or Sarjeant (Ref. C4) for the (v₁, v₃) reservoir relaxation were not based on experimental evidence specific to either Reaction C2 or C3.

The Finzi et al. room temperature rate constants of 4.6×10^{-13} and 3.3×10^{-13} cm³ molecule⁻¹ s⁻¹ for N₂ and O₂, respectively, were already incorporated into the kinetics scheme of earlier versions of SHARC, and, therefore, we have not recommended any changes.

b) Relaxation of H₂O(110) and H₂O(011) Combination Levels by O₂ and N₂

The following V-R,T energy transfer processes from combination levels are included in the H₂O kinetics scheme used in SHARC:



with M = O₂ or N₂. The energy difference between the v₁+v₂ level and the v₂+v₃ level is only 96 cm⁻¹. Therefore, rapid energy exchange will occur between the two levels, and they can be treated as a reservoir. Furthermore, processes 4 and 5 are analogous to processes 2 and 3 described in Part (a) of this appendix, that is, $k_2 \approx k_3 \approx k_5 \approx k_6$. A common room temperature rate constant is recommended. Again, the rate constants for N₂ and O₂ are differentiated by the efficiency factors of 1.0 and 0.7.

c) V-T Relaxation of the v₁ and v₂ Levels by Atomic Oxygen

The rate constant for processes C3 and C4 with O(³P) as the collision partner was measured by Zittel et al. (Ref. C5) at 315 K and 520 K using laser-induced fluorescence. The experimental values were $3(\pm 2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ and $5(\pm 3) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, respectively. There is insufficient data to establish a temperature trend so an average rate constant of 4×10^{-12} cm³ molecule⁻¹ s⁻¹ is recommended. In Table 1, the rate constant is reported as a collision efficiency parameter to the rate constant for Reaction C1.

The 1976 Standard model atmosphere (Ref. C6) indicates that at altitudes where O(³P) becomes a significant atmospheric constituent, the number density of H₂O has decreased to the extent that collisional relaxation of vibrationally excited H₂O by atomic oxygen is not

competitive with similar mechanisms involving N_2 or O_2 . This conclusion is based on combining typical number densities for H_2O and $O(^3P)$ with the average rate constant for processes C3 and C4.

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APPENDIX D

RATE CONSTANTS FOR SPONTANEOUS EMISSION PROCESSES FROM VIBRATIONALLY EXCITED H₂O

The 1991 HITRAN sum-of-lines band strengths (Ref. D1) given in Column 3 of Table D1 were used to calculate the Einstein A coefficients for spontaneous emission (in units of s⁻¹). The formula used for the calculation is that used in the SHARC 2.0 manual (Ref. D2) and in Ref. D3. That is,

$$A = \frac{8\pi c \nu^2 S_{ul}}{g_u} \frac{\exp[E_l/205.727]}{1 - \exp[-\nu/205.727]} \quad (D1)$$

where ν is the transition frequency in cm⁻¹ and E_l is the lower state energy in cm⁻¹. These and the other variables are described in references D2 and D3 as well as in the first report of this series (TR-0091(6078)-1). The units for S_{lu} are cm⁻¹/molecule/cm² or cm/molecule.

A comparison of our calculated A values and those used in earlier versions of SHARC indicated several discrepancies. Several of these differences were $\leq 10\%$. However, the $\nu_1 - 0$, $3\nu_2 - 0$, $2\nu_2 - \nu_2$, $\nu_1 - \nu_2$, and $\nu_3 - \nu_2$ Einstein A values were in much worse agreement. It appears that some of the spontaneous emission rate constants used in SHARC could have been derived from the dipole moments reported in the original references. The Einstein A coefficient calculated from the basic formula containing the transition moment R^{nm} and the frequency of the transition, ν , is (Ref. D4)

$$A = \frac{64\pi c \nu^3}{(4\pi\epsilon_0) 3hc^3} |R^{nm}|^2 \quad (D2)$$

The latter calculation is complicated when there are Fermi interactions or Coriolis effects occurring. This is the case for the two sets of triad levels in H₂O. The interacting levels are ν_1 , ν_3 , and $2\nu_2$ in one set; and $3\nu_2$, $\nu_1 + \nu_2$, and $\nu_2 + \nu_3$ for the second set. Therefore, it is necessary to use a transformed dipole moment operator that includes a rotational operator, and a set of vibration-rotation wavefunctions for all three levels of the triad. The approximation that $|R^{nm}|^2 = |\mu|^2$ results in the A coefficients in Column 6 of Table D1. We did not pursue the detailed calculations involved for some of the other vibrational transitions via the dipole moment method.

Since Rothman's band strengths contain the best literature values to date for the rovibrational line strengths and, thus, the sum-of-line strengths, our recommendation is to standardize the Einstein A coefficients in the code by calculating them from Eqn. D1.

Table D1. Einstein A Coefficients for H₂O Vibrational Levels

BAND	Band Center Frequency (cm ⁻¹)	HITRAN Sum of Lines(D1) cm ⁻¹ /(molecule cm ⁻²)	Einstein A from Sum of Lines (s ⁻¹)	Dipole Moment μ (D)	Einstein A Calculated from μ (s ⁻¹)	SHARC 2.0 A (s ⁻¹)
ν_1	3657.08(D5)	4.96 x 10 ⁻¹⁹	5.00	-0.1532(D7)	3.61	3.37
ν_2	1594.74(D6)	1.06 x 10 ⁻¹⁷	20.33	0.1269(D6)	20.47	18.35
ν_3	3755.92(D5)	7.20 x 10 ⁻¹⁸	76.58	0.0686(D7)	78.34	78.40
2 ν_2	3151.63(D5)	7.57 x 10 ⁻²⁰	0.567	0.00581(D7)	---	0.454
3 ν_2	4666.8(D9)	3.96 x 10 ⁻²²	0.0065	0.209 x 10 ⁻⁴ (D8)	---	0.003
$\nu_1 + \nu_2$	5235.0(D9)	3.72 X 10 ⁻²⁰	0.768	-0.002578(D8)	0.300	0.349
$\nu_2 + \nu_3$	5331.279(D9)	8.04 x 10 ⁻¹⁹	17.23	-0.019563(D8)	18.25	17.22
2 ν_2 - ν_2	1556.89	9.71 x 10 ⁻²¹ (lit. 8.15 x 10 ⁻²¹)(D11)	41.29 34.65	0.1794(D11)	---	33.74
ν_1 - ν_2	2062.34	1.82 x 10 ⁻²²	1.36	0.447 x 10 ⁻² (D11)	---	0.612
ν_3 - ν_2	2161.18	2.63 x 10 ⁻²²	2.15	0.0267(D11)	---	3.70
3 ν_2 - ν_2	3072.06	7.30 x 10 ⁻²³	1.21	---	---	1.11
($\nu_1 + \nu_2$) - ν_2	3640.26	1.95 x 10 ⁻²²	4.53	---	---	4.17
($\nu_2 + \nu_3$) - ν_2	3736.54	2.92 x 10 ⁻²¹	71.49	---	---	65.98
3 ν_2 - 2 ν_2	1515.17	5.14 x 10 ⁻²⁴	40.06	---	---	36.87

Superscripts [e.g., (D8)] refer to References D1 through D11.

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