JOURNAL OF SPACECRAFT AND ROCKETS
Vol. 30, No. 6, November–December 1993

Analysis of HAVE SLED II Flight Test Water Outgassing

James W. Duff,* Steven C. Richtsmeier,* and Lawrence S. Bernstein†
Spectral Sciences, Inc., Burlington, Massachusetts 01803
and
Hsiao Hua K. Burke‡ and Maryanne Pietrzyk§
MIT Lincoln Laboratory, Lexington, Massachusetts 02173

Water outgassing at altitudes greater than 250 km was observed during the Lincoln Laboratory HAVE SLED II series of sounding rocket experiments. The major spectral features include the water ν_2 band at 6.3 μm and rotational emission at wavelengths greater than 15 μm. These data contain information on the rotational and ν_2 vibrational temperatures, as well as the water outgassing rate. An analytical model has been developed to predict the long wavelength infrared spectral radiance from the outgassing of water from a vehicle surface. An outgassing rate of 0.3–3 g/s of H_2O was determined to be consistent with the data. The H_2O rotational and vibrational temperatures were estimated to be 220 ± 30 K and 265 ± 30 K, respectively.

Nomenclature

A_u = spontaneous emission rate from excited state u, s^{-1}
A_{ul} = spontaneous emission rate from excited state u to lower state l, s^{-1}
c = speed of light, 2.998×10^8 m/s
c_2 = second radiation constant, 1.439 cm K
E_r = rotational energy, cm^{-1}
E_v = vibrational energy, cm^{-1}
E_2 = second exponential integral
g_l = degeneracy of lower state l
g_u = degeneracy of excited state u
h = Planck constant, 6.63×10^{-34} J s
I_{ul} = line-of-sight radiance for transition $u \rightarrow l$, W/cm^2/sr
$I_{ul}(R)$ = volumetric radiance for transition $u \rightarrow l$, W/cm^3/sr
k = Boltzmann constant, 1.381×10^{-23} J K^{-1}
m = mass of H_2O, g/molecule
P_l = relative population of lower state l
P_u = relative population of excited state u
Q_e = Earthshine contribution to the line-of-sight radiance
Q_t = thermal contribution to the line-of-sight radiance
Q_{vr} = vibrational-rotational partition function
R = radial distance from the outgassing source, m
R_0 = effective radius of outgassing source, m
T_e = effective Earthshine temperature for the $l \rightarrow u$ transition, K
T_r = rotational temperature, K
T_{re} = effective rotational temperature due to Earthshine excitation, K
T_s = vehicle surface temperature, K
T_t = translational temperature, K
T_v = vibrational temperature, K
T_{ve} = effective vibrational temperature due to Earthshine excitation, K
v = radial velocity, m/s
w = mass flow rate, g/s
$\rho(R)$ = total number density, g/cm^3
$\rho_u(R)$ = excited state number density, g/cm^3
ω_{ul} = frequency of transition $u \rightarrow l$, cm^{-1}

Introduction

MOLECULAR emission resulting from the outgassing of contaminants condensed on space vehicle surfaces may seriously degrade the performance of optical systems by providing background radiation which may exist throughout the infrared spectral region. In particular, water can be a major contamination source for a number of reasons. Atmospheric water may condense on cryogenic surfaces prior to launch, and it may also be absorbed by a variety of porous materials used as protective coverings or in the construction of payload instrumentation. As a general rule, the water outgassing rate decreases as a function of time after launch. It is important to characterize both the absolute water outgassing rate, as well as its temporal behavior, to assess the potential for interference with sensitive infrared (IR) measurements from space platforms.

Water outgassing at altitudes greater than 250 km was observed during the HAVE SLED II series of sounding rocket experiments. The major spectral features include the water ν_2 band at 6.3 μm and rotational emission at wavelengths greater than 15 μm. These data contain information on the rotational and ν_2 vibrational temperatures, as well as the water outgassing rate.

There are relatively few quantitative determinations of water outgassing rates from space vehicles. From the Space Shuttle mission STS-4, the time-dependent H_2O mass ejection rate was derived from analysis of mass-spectrometric data.[1] The H_2O mass flow rate was found to occur on two time scales.[2] The fastest rate was 0.3 g/s with a 5.9-h characteristic decay time (i.e, the time it takes the rate to fall to $1/e$ of its initial value), and the slowest rate was 0.02 g/s with a 54-h decay time. An analysis[3] of measurements of ionic species in the Space Shuttle bay has also provided an upper bound to the H_2O outgassing rate of approximately 0.4 g/s. Unfortunately, there were no data taken on the time scale of minutes after launch, which would offer the most meaningful comparison to the HAVE SLED II data. However, such data are available from the EXCEDE:SPECTRAL sounding rocket experiment.[4] This experiment utilized electron beams to simulate an artificial aurora in the 60–130 km altitude regime. During periods when the electron beams were off, large H_2O ν_2 6.3 μm and rotational emissions were observed with a circular variable filter (CVF) spectrometer. Analysis of these data indicated an H_2O outgassing rate of approximately 1 g/s, with a decay time constant of 100 s. Laboratory measurements[5] of H_2O outgassing in a vacuum from clean surfaces typically show rates on the order of 10^{-3} g/s-m^2, which are reasonably consistent with the Shuttle observations but much lower than

---

Received Oct. 22, 1992; revision received Jan. 5, 1993; accepted for publication Jan. 5, 1993.

*Principal Scientist.

†Chief Scientist.

‡Assistant Group Leader.

§Staff Member.

observed during the EXCEDE experiment. However, sounding rocket flights may be equipped with cryogenic instrumentation, which could be a major contributor to the large outgassing rates.

An analytical model is developed in this paper to predict the long wavelength infrared (LWIR) spectral radiance from water which has outgassed from a vehicle surface. The radiation mechanism considered here is thermal vibrational-rotational emission determined by the vehicle surface temperature. A previous model[2] developed by Young and Herm also considered the vibrational excitation of ejected molecules by Earthshine and sunshine radiation and by hyperthermal collisions with the ambient atmosphere. However, these two additional sources of radiation are unimportant in the present study because 1) the sensor field of view (FOV) used in the present study is much larger than that considered by Young and Herm, thus, discriminating against Earthshine and solar excitation and 2) O + H_2O collision velocities were too low during the HAVE SLED II flights for collisional excitation to be important.

HAVE SLED II Data

The HAVE SLED II sounding rocket program was conducted in 1983–1984 at the Poker Flat Research Range, Alaska, by MIT/Lincoln Laboratory. The major objective of the program was to measure the LWIR signatures of various targets against a space background. One of the primary instruments on the payload module was a circular variable filter spectrometer covering the wavelength range of 5–22 μm with a 2% spectral resolution and a 4-deg × 4-deg field of view. This paper focuses on the spectral data obtained during periods when no targets were being observed. Emissions from outgassed water were observed beginning at 160 s after launch for a duration of approximately 160 s over an altitude range of 250–400 km.

Contaminant outgassing was observed in the CVF spectra throughout the LWIR. Representative data illustrating the contaminant radiation is shown in Fig. 1. Spectral features near the noise level of the instrument were enhanced by averaging 65 CVF scans. Spectral features observed include water ν_2 emission at 6.3 μm, rotation at wavelengths greater than 15 μm, and emission from unidentified radiator(s) at 9 and 12.5 μm. Emission at 12.5 μm has been observed during other sounding rocket flights and has been tentatively associated with silicone greases and adhesives.[6]

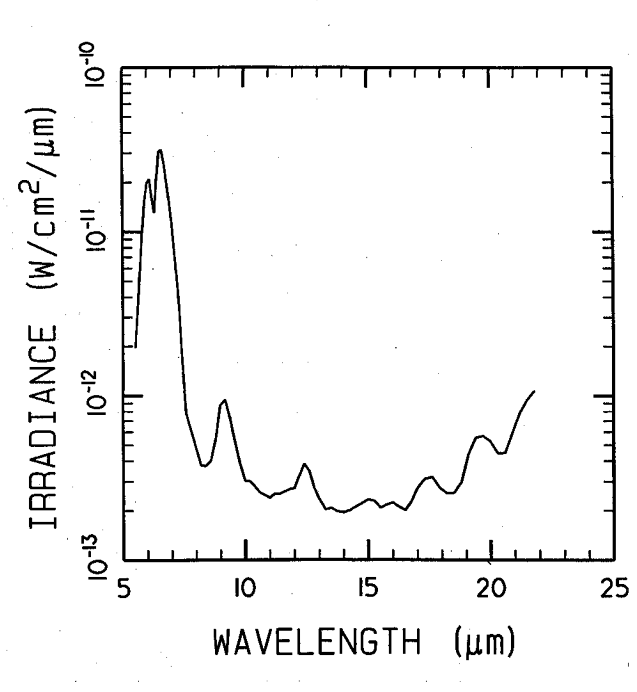

Fig. 1 Average of 65 HAVE SLED II LWIR spectra.

The water emissions were essentially constant over the 160-s observation period, which included a solar terminator crossing. Thus, solar excitation does not contribute to the observed emissions. In addition, the observations were made as the rocket approached apogee, so the relative velocity between the outgassing H_2O and the ambient atmospheric species was insufficient to collisionally excite water.[7] Also, estimates of the natural atmospheric water background radiance are many orders of magnitude below the observed radiance. Thus, the most likely source of the observed radiance is thermal emission from outgassing water molecules. In the next section, a radiation model is developed to describe the thermal emissions.

Radiation Model

The main source of the LWIR contamination observed during the HAVE SLED II experiment is thought to be due to thermal emission from H_2O molecules leaving the vehicle surface. To model the outgassing process, molecules are assumed to be released uniformily at a constant velocity from a point source centered at the vehicle. The ejected molecules do not interact with each other and they emit radiation from excited vibrational-rotational states. There are many different surfaces, both external and internal, from which the water may be outgassing, and there may be a wide range of surface temperatures to consider. We make the simplification that the outgassing can be represented as arising from an "effective" single, spherical surface with a temperature approximating that of the payload area of the HAVE SLED vehicle, 290 K. The excited state population is initially determined by, but not necessarily equal to, the surface temperature. Only the emission of the first photon from an excited molecule is considered in the present model. Emission of subsequent photons from molecules which are still in an excited state will occur at distances sufficiently far from the sensor so as to be of secondary importance.

The H_2O number density from a point source is given by

$$\rho(R) = w/4\pi R^2 v \tag{1}$$

Although there is a singularity in the density at $R = 0$, the density is only used for $R > R_0$, where R_0 is the effective "spherical" radius of the outgassing source. The vehicle dimensions provide an upper bound for R_0. For the present application, a value of 0.5 m has been assumed for R_0. The radial velocity is taken to be the average speed assuming a Maxwellian flux distribution at a translational temperature and is given by

$$v = (9\pi k T_t / 8m)^{1/2} \tag{2}$$

The translational temperature is assumed to be 40% of the vehicle surface temperature, based on measured translational energy distribution of D_2O desorbing from polycrystalline platinum surfaces,[8] resulting in a translational temperature of 116 K. The corresponding mean velocity from Eq. (2) is 435 m/s. The excited state number density as a function of radial distance is

$$\rho_u(R) = \rho(R) P_u(T_v, T_r) e^{-A_u(R - R_0)/v} \tag{3}$$

The exponential term represents the fraction of molecules remaining in the excited vibrational-rotational state at distance R. The spontaneous transition probabilities are calculated from the 1986 Geophysics Laboratory HITRAN line atlas.[9] The relative population of the initially desorbed excited state molecule at a particular vibrational temperature and rotational temperature is

$$P_u(T_v, T_r) = g_u \exp[-c_2(E_v/T_v + E_r/T_r)]/Q_{vr}(T_v, T_r) \tag{4}$$

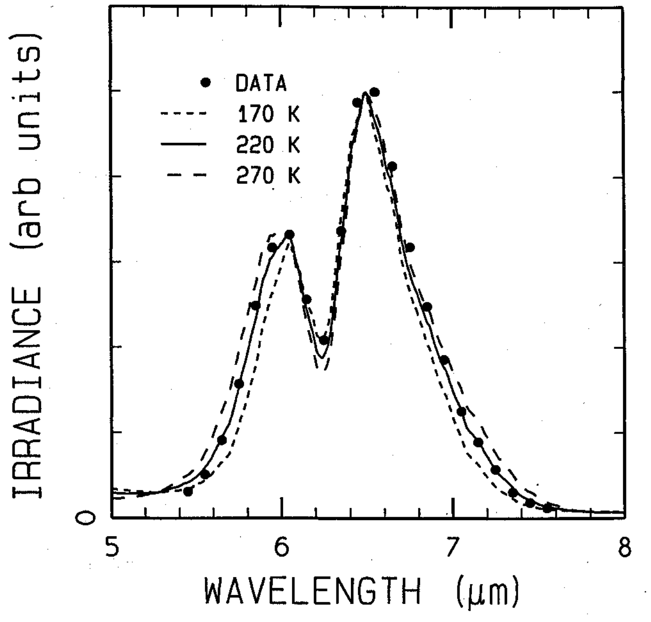

Fig. 2 Comparison of H_2O 6.3-μm HAVE SLED II spectrum with model calculations for several rotational temperatures.

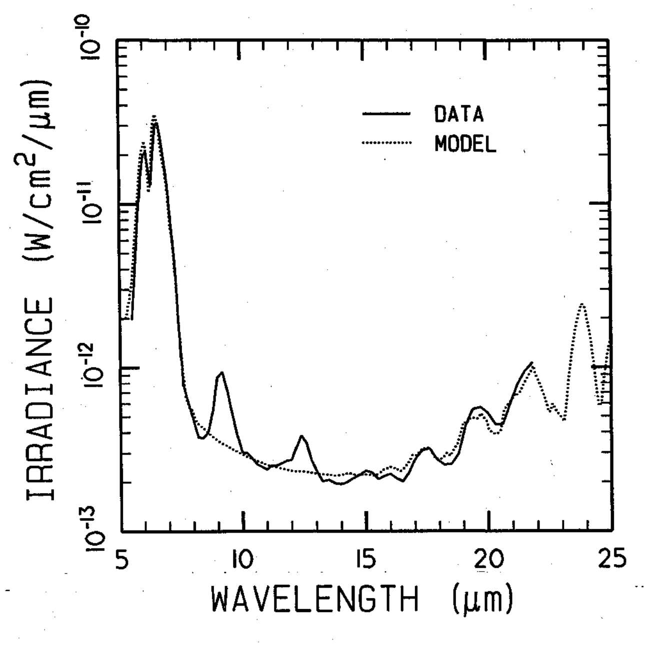

Fig. 3 Comparison of the H_2O spectral outgassing model with the HAVE SLED II data.

where the vibrational-rotational partition function is given by

$$Q_{vr}(T_v,T_r) = \Sigma\, g_u \exp[-c_2(E_v/T_v + E_r/T_r)] \qquad (5)$$

with the sum extending over all vibrational-rotational states.

The volumetric radiance at any point in space is given by

$$I_{ul}(R) = (hc/4\pi)\, \omega_{ul} A_{ul} \rho_u(R) \qquad (6)$$

where $hc\omega_{ul}$ is the photon energy for the $u \rightarrow l$ transition. The radiance observed by the sensor is obtained by integrating the volumetric radiance along the specified line of sight (LOS)

$$I_{ul} = \int_{R_0}^{\infty} I_{ul}(R)\mathrm{d}R \qquad (7)$$

Performing the integral in Eq. (7) gives

$$I_{ul} = \frac{hcw}{16\pi^2 vR_0}\, \omega_{ul} A_{ul} Q_t \qquad (8)$$

The quantity Q_t represents the contribution of the thermal (surface) excitation to the radiance,

$$Q_t = P_u(T_v, T_r) E_2(R_0 A_{ul}/v) e^{A_u R_0/v} \qquad (9)$$

Note that I_{ul} is almost inversely proportional to the parameter R_0.

The Earthshine contribution,[2] although not important for the present application, can be included in the model using the approximation

$$Q_e = P_l(T_{ve}, T_{re}) C_{ul}(\omega_{ul}, T_e)\{1 - E_2(R_0 A_{ul}/v)\} \qquad (10)$$

where the lower state population is determined at an effective vibrational and rotational temperature due to Earthshine pumping and $C_{lu}(\omega_{ul}, T_e)$ is related to the incident Earthshine radiance (neglecting the curvature of the Earth)

$$C_{lu}(\omega_{ul}, T_e) = \frac{1}{2}\,\frac{g_u}{g_l}\,\frac{1}{e^{c_2\omega_{ul}/T_e} - 1} \qquad (11)$$

The Earthshine contribution to I_{ul} is then obtained by adding Q_e to Q_t in Eq. (8).

The I_{ul} calculated from Eq. (8) represents the spectral radiance for a particular vibrational-rotational transition. A spectrum is obtained by "histograming" the I_{ul} for the calculated transition frequency into finite spectral bins. To compare the model with the HAVE SLED II data, the calculated spectral radiance was spectrally degraded to the resolution of the CVF and multiplied by the CVF FOV (4.83×10^{-3} sr) to convert to a spectral irradiance (W/cm²/μm).

A comparison of this model with the HAVE SLED II spectral data allows the determination of the initial H_2O vibrational and rotational temperatures, as well as the outgassing rate. Such an analysis is performed in the following section.

HAVE SLED II Data Analysis

The H_2O rotational temperature of the spectrum shown in Fig. 1 can be estimated by comparing the shape of the 6.3-μm

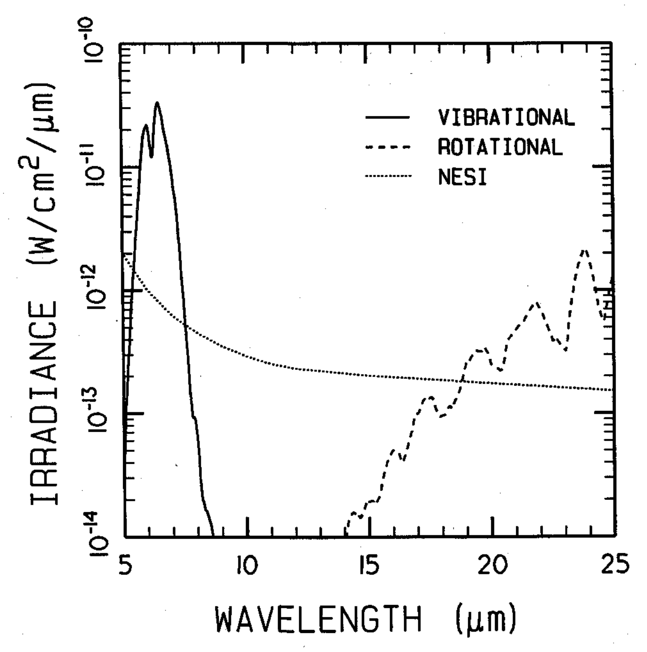

Fig. 4 Vibrational, rotational, and noise equivalent spectral irradiance (NESI), components of the H_2O outgassing model.

band to the spectral model for a range of rotational temperatures. Comparison of the 6.3-μm data with the spectral model is shown in Fig. 2, resulting in an estimated rotational temperature of 220 ± 30 K. It is common practice to characterize the energy exchange which takes place on a surface by defining an accommodation coefficient, with a value of unity corresponding to complete thermalization. Of course, the concept of an accommodation coefficient assumes that the distribution of excited states is determined by the surface interaction, and not by H_2O-H_2O collisions in the outgassing cloud. Based on a surface temperature of 290 K, the deduced rotational temperature corresponds to an accommodation coefficient for rotation of 0.75 ± 0.1. This value is consistent with accommodation coefficients measured in a variety of surface experiments for different molecules.[10] The ν_2 vibrational temperature can be obtained by adjusting the ratio of water rotational emission to the 6.3 μm ν_2 emission until the ratio agrees with the data. Using the rotational temperature of 220 ± 30 K just determined, a vibrational temperature of 265 ± 30 K is obtained. The corresponding accommodation coefficient for ν_2 is then 0.90 ± 0.1, again consistent with laboratory measurements.[10] The observation that vibration is more completely accommodated than rotation is in agreement with other laboratory measurements.[10]

Specifying the rotational and vibrational temperatures completely determines the shape of the H_2O spectrum predicted by the model [Eq. (8)]. The outgassing rate is determined by adjusting the calculated absolute intensity to agree with the data shown in Fig. 1. Using rotational and vibrational temperatures of 220 and 265 K, respectively, a water outgassing rate of 0.9 g/s is required to be consistent with the data. The predicted spectrum using these model parameters is compared to the HAVE SLED II data in Fig. 3. The noise equivalent spectral irradiance of the CVF spectrometer has been added to the model spectrum. The various components which comprise the outgassing spectral model are illustrated in Fig. 4.

It can be seen that all of the H_2O spectral features in the data are predicted remarkably well by the model. Of course, the remaining unidentified contamination features at 9 and 12.5 μm are not included in the model. The uncertainty in the rotational and vibrational temperatures results in a range of possible outgassing rates of 0.3–3 g/s. This range of outgassing rates implies a total mass of 100–1000 g of H_2O desorbing from the vehicle surface during the observation.

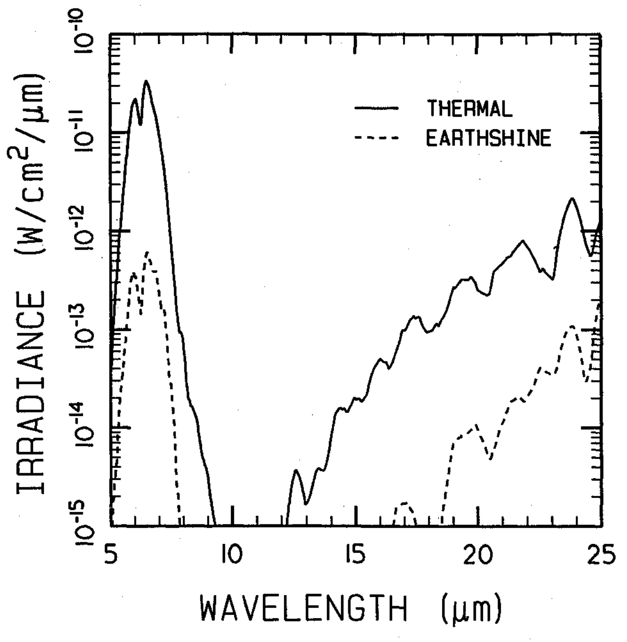

Fig. 5 Relative importance of thermal and earthshine excitation.

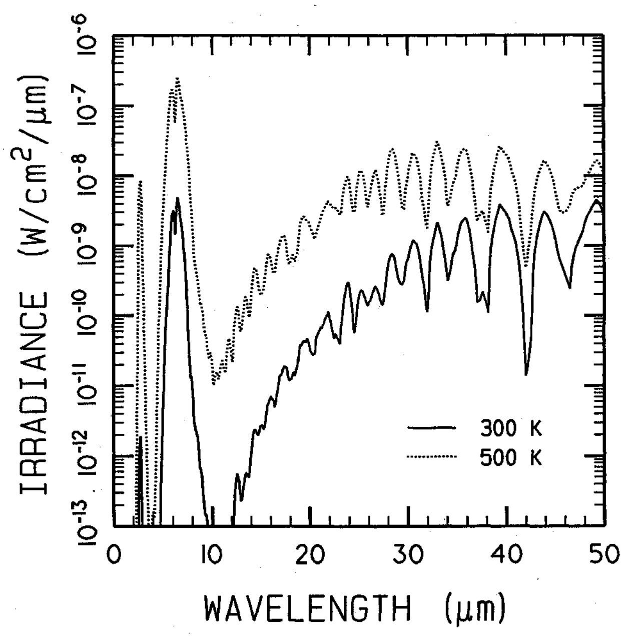

Fig. 6 Dependence of the H_2O radiance on the surface temperature.

It was stated that Earthshine excitation was a relatively unimportant excitation mechanism for the HAVE SLED II data. Qualitatively, the relative contributions of the thermal and Earthshine excitation can be estimated from Eqs. (9) and (10). The thermal excitation is proportional to the $E_2(x)$ function, whereas Earthshine excitation is proportional to $1 - E_2(x)$. The second exponential function represents the convolution of the r^{-2} falloff of excited state number density with the spontaneous emission rate. Small values of x ($= R_0A_{ul}/v$) favor thermal excitation over Earthshine excitation. For H_2O 6.3-μm emission, x is typically less than 0.05, which means that significant emission occurs within approximately 20 m of the vehicle surface. In other words, thermal excitation is important in the near field where the density of excited state molecules is high, and Earthshine excitation is important in the far field where excited state density is low. Thus, for Earthshine emission to be detected, a narrow FOV sensor would have to be used, which would effectively discriminate against thermal emission. The relative importance of the thermal and Earthshine excitation mechanisms is shown in Fig. 5 for the HAVE SLED II circular variable filter field of view. For the Earthshine excitation mechanism, an effective Earthshine temperature for vibrational and rotational excitation was assumed to be 250 K, which is probably an upper bound.[2] The contribution of Earthshine excitation to the outgassing signature is less than 5% throughout the infrared spectral region.

Discussion

It is difficult to assess the relationship of the outgassing rate implied by the HAVE SLED II data to other outgassing measurements. Apparently, the only other relevant measurement in space is the EXCEDE:SPECTRAL measurement,[4] although the altitude range covered by EXCEDE:SPECTRAL (60–130 km) is substantially lower than the HAVE SLED II experiment (250–400 km). Nevertheless, the outgassing rate of 0.9 g/s determined in the present study is similar to the previous sounding rocket experiment. The time scale of the outgassing experiment performed from the Shuttle mission STS-4 (Ref. 2) precludes a meaningful comparison with sounding rocket measurements.

The determination of vibrational and rotational distributions (i.e., temperatures) of H_2O from a surface in space makes the HAVE SLED II analysis unique. Although vibrational and rotational accommodation coefficients of polyatomic molecules have been measured in the laboratory only for CO_2 and OCS, the vibrational and rotational accommodation coefficients obtained from the HAVE SLED II data are consistent with those for CO_2 and OCS.

It is interesting to consider wavelength regions outside those considered in the preceding sections. For this purpose, radiance calculations shown in Fig. 6 were performed using a 1-g/s outgassing rate with vehicle surface temperatures of 300 and 500 K, assuming temperature-independent vibrational and rotational accommodation coefficients. For the $H_2O(\nu_1, \nu_3)$ emission at 2.7 μm, vibrational temperatures were assumed to be the same as $H_2O(\nu_2)$. Increasing the surface temperature from 300 to 500 K for a constant outgassing rate results in increased emission throughout the wavelength regime, with the most significant increase at the shorter wavelengths (again due to the Boltzmann population factor). As expected, emission at 2.7 μm is several orders of magnitude lower than emission at 6.3 μm, due to the Boltzmann population factor [Eq. (4)]. For H_2O rotations, the emission increases by a factor of 5 from 20 to 30 μm and remains relatively constant for wavelengths greater than 30 μm.

Although the present radiation model contains much of the physics of the outgassing phenomenon, there are several model improvements which should result in a more accurate description of the HAVE SLED II outgassing rate. The most significant model upgrade would be a more accurate description of the vehicle geometry and its effect on the density of outgassed molecules, including the actual vehicle dimensions and location of the CVF spectrometer. Only the absolute radiance and the derived outgassing total mass flow, not the spectral shape, would be affected by this improvement. Of lesser importance would be the multiphoton emission from the cascading of high lying rotational states, which would affect the spectral shape. This effect would perhaps be more important at wavelengths longer than those considered in the present analysis.

Summary

The HAVE SLED II data have provided a unique spectral data base for H_2O outgassing. A spectral model for thermal emission from molecular contaminants was used to analyze the data. An outgassing rate of 0.3–3 g/s of H_2O was determined to be consistent with the data. The H_2O rotational and vibrational temperatures were estimated to be 220 ± 30 K and 265 ± 30 K, respectively. These temperatures correspond to accommodation coefficients of 0.75 ± 0.1 and 0.90 ± 0.1, for rotation and vibration, respectively.

Acknowledgments

This work was sponsored by the Applied Physics Laboratory at the Johns Hopkins University under Subcontract APL 605361-S. The authors are grateful to Robert Erlandson and Phillip Joyce for their continued interest and support of this work. The HAVE SLED II flight test was conducted by the Army Strategic Defense Command in 1984.

References

[1] Green, B. D., Caledonia, G. E., and Wilkerson, T. D., "The Shuttle Environment: Gases, Particulates, and Glow," *Journal of Spacecraft and Rockets,* Vol. 22, No. 5, 1985, pp. 500–511.

[2] Young, S. J., and Herm, R. R., "Model for Radiation Contamination by Outgassing from Space Platforms," *Journal of Spacecraft and Rockets,* Vol. 25, No. 6, 1988, pp. 413–419.

[3] Caledonia, G. E., Person, J. C., and Hastings, D. E., "The Interpretation of Space Shuttle Measurements of Ionic Species," *Journal of Geophysical Research,* Vol. 92, No. A1, 1987, pp. 273–281.

[4] Bien, F., and Bernstein, L. S., "Infrared Signatures Due to Water Contamination on EXCEDE:SPECTRAL," *Proceedings of the 1986 Meeting of the IRIS Specialty Group on Targets, Backgrounds, and Discrimination* (San Diego, CA), Vol. 2, July 1987, pp. 183–203.

[5] Glassford, A. P. M., and Garett, J. W., "Characterization of Contamination Generation Characteristics of Satellite Materials," Wright Research and Development Center, WRDC-TR-89-4114, Wright-Patterson AFB, OH, Nov. 1989.

[6] Smith, D. R., private communication, Phillips Lab., Geophysics Directorate, Bedford, MA, Oct. 1988.

[7] Johnson, B. R., "A Quantum Mechanical Investigation of Vibrational Energy Transfer in $O(^3P) + H_2O$ Collisions," *Journal of Chemical Physics,* Vol. 84, No. 1, 1986, pp. 176–180.

[8] Ceyer, S. T., Guthrie, W. L., Lin, T.-H., and Somorjai, G. A., "D_2O Product Angular and Translational Energy Distributions from the Oxidation of Deuterium on Pt(111)," *Journal of Chemical Physics,* Vol. 78, No. 11, 1983, pp. 6982–6991.

[9] Rothman, L. S., Gamache, R. R., Goldman, A., Brown, L. R., Toth, R. A., Pickett, H. M., Poynter, R. L., Flaud, J. M., Camy-Peyret, C., Barbe, A., Husson, N., Rinsland, C. P., and Smith, M. A. H., "The HITRAN Database: 1986 Edition," *Applied Optics,* Vol. 26, No. 19, 1987, pp. 4058–4097.

[10] Houston, P. L., and Merrill, R. P., "Gas-Surface Interactions with Vibrationally Excited Molecules," *Chemical Reviews,* Vol. 88, No. 4, 1988, pp. 657–671.

Alfred L. Vampola
Associate Editor