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Research Paper

Search for the OH ($X^2\Pi$) Meinel Band Emission in Meteors as a Tracer of Mineral Water in Comets: Detection of N_2^+ (A-X)

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ABSTRACT

We report the discovery of the N_2^+ *A-X* Meinel band in the 780–840 nm meteor emission from two Leonid meteoroids that were ejected less than 1,000 years ago by comet 55P/Tempel-Tuttle. Our analysis indicates that the N_2^+ molecule is at least an order of magnitude less abundant than expected, possibly as a result of charge transfer reactions with meteoric metal atoms. This new band was found while searching for rovibrational transitions in the $X^2\Pi$ electronic ground state of OH (the OH Meinel band), a potential tracer of water bound to minerals in cometary matter. The electronic *A-X* transition of OH has been identified in other Leonid meteors. We did not detect this OH Meinel band, which implies that the excited *A* state is not populated by thermal excitation but by a mechanism that directly produces OH in low vibrational levels of the excited $A^2\Sigma$ state. Ultraviolet dissociation of atmospheric or meteoric water vapor is such a mechanism, as is the possible combustion of meteoric organics. Key Words: Prebiotic molecules—Origin of life—Meteors—Molecular band emission. Astrobiology 4, 109–121.

INTRODUCTION

THE SEARCH FOR WATER in non-terrestrial environments is a driving force in astrobiology. Life on Earth is intimately associated with liquid water to the extent that any environment in which liquid water can exist appears to be a suitable habitat for life. A late veneer of comet or hydrated asteroid impacts is hypothesized as the source of oceanic water on Earth (Oró, 1961; Chyba and Sagan, 1992, 1997; Delsemme, 1992; Brack, 1999). Understanding the origin of our oceans is important for understanding the potential for life on other planets.

The most obvious source of oceanic water (H_2O molecules, perhaps derived from hydrogen and oxygen in other forms) are giant impacts of comets, which contain ~30% water ice. However, water ice in comets like 1P/Halley that are thought to originate in the Uranus–Neptune re-

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gion have a D/H ratio that is twice the value of that of our ocean water (*e.g.,* Reber, 1996). Only recently has a comet, C/1999 S4 (LINEAR), been observed with the same D/H ratio as ocean water, suggesting that the cometary ice came from objects formed closer to the Sun, perhaps from a reservoir that smoothly transitions into the asteroid belt (Mumma *et al.,* 2001). Because their D/H ratio is similar to that of ocean water, asteroids are often implicated in having delivered water to Earth in a form bound in layer lattice silicates. All layer lattice silicates contain OH groups, and the smectite group minerals, also known as swelling clays, are capable of incorporating layers of water into their structure.

A continuous bombardment by meteoroids, the product of comet outgassing and asteroid collisions, can also have delivered the water of our oceans. Interlayer and structural water would not be lost from a meteoroid when exposed to the vacuum in space. Cometary dust also contains OH groups and hydrogen with anomalous D/H ratios incorporated in refractory organic matter (Messenger, 2000). That delivery could have taken the form of micrometeorites (Maurette *et al.,* 2000) or in gaseous form after ablation in the atmosphere (Jenniskens *et al.,* 2000a). Indeed, a small fraction of the asteroidal meteoroids in micrometeorite collections are composed of CI meteorites, heavily hydrated rocks of asteroidal origin (Greshake *et al.,* 1998; Maurette, 1998), which likely originated from a recent collision in the asteroid belt (Dermott *et al.,* 2003). However, the bulk of infalling mass is ablated in the atmosphere. Meteoroids 10–50 μm in size that have low enough impact speeds can effectively radiate the heat from air collisions. Large meteoroids have lower speeds. Recovered micrometeorites 35–50 μm in size have entry speeds close to the lower limit of 11.1 km/s that results from falling into Earth's gravitational well (Flynn, 1995). However, orbital surveys of radar meteors indicate that the present-day peak of the mass influx is dominated by even larger (~150 μm) grains on cometary orbits that enter Earth's atmosphere at much faster speeds ($\geq$25 km/s) (Galligan and Baggaley, 2001). Such grains do not survive atmospheric entry intact.

Water in cometary dust?

It is unknown if cometary grains contain water. Once released from a comet, water ice is not expected to survive exposure to the vacuum of space when approaching as close to the Sun as Earth's orbit [$T_{\max}$ ~250–300 K (Levasseur-Regourd *et al.,* 2000)]. Only water bound to minerals remains, which may have a different D/H ratio than the water ice. If the D/H ratio of water in minerals is less than that in cometary ice, then even Halley-type comets were a source of our ocean water.

The case for mineral water in cometary dust is weak. To hydrate "swelling" clays, liquid water is needed. It has been argued that transient pockets of liquid water may exist in active comet nuclei, because of possible sources of energy that warm the water ice under pressure (Prialnik and Podolak, 1995; Borucki *et al.,* 2002).

After 20 years of laboratory analyses of interplanetary dust particles, debates about whether cometary dust is completely anhydrous persist (Rietmeijer, 1998). Mid-infrared (IR) spectra of comet dust indicate that layer lattice silicates are not an important component of cometary dust (Hayward *et al.,* 2000). Mass spectroscopic analysis of 1P/Halley dust grains probed during the GIOTTO and VEGA missions (Kissel and Krueger, 1987; Jessberger and Kissel, 1991) did not conclusively eliminate the possibility that the silicate fraction could contain hydrogen (in the form of OH or H_2O). Indeed, the combination of spectral signatures and the mass of individual Halley particles led Rietmeijer *et al.* (1989) to conclude that layer lattice silicates were present in this comet. Unfortunately, each of these techniques samples only relatively small ($<<$100 μm) grains.

Water can also be adsorbed on minerals or trapped in pores, which would not be detectable in mid-IR spectra if the meteoroids are significantly larger than the wavelength of the OH stretch vibration band ($>>$3 μm) and the Si-O stretch vibration band ($>>$10 μm). Currently, there is no observational or experimental evidence that indicates that water exists in the pores of meteoroid grains. However, this remains an interesting hypothesis. Water trapped in pores could be lost during atmospheric entry and by subsequent exposure to the Earth environment before grains are collected in the atmosphere. Indeed, high altitude emission from meteors observed when the meteoroids are less than 500 K warm has been interpreted as due to the loss of "water of hydration" (Cook *et al.,* 1973).

OH emission in meteor spectra of large cometary dust grains

In this context, it is important to note that several tentative identifications have been made of the 310 nm OH *A-X* (0,0) emission in the spectra of meteors caused by relatively large ~5-mm-sized cometary dust grains. From two-channel photometric data, Harvey (1977) reported an excess of emission at 310 nm in a Perseid and an α-Capricornid shower meteor, which sample cometary dust. The first ultraviolet (UV) spectrum of a −2 magnitude Leonid, observed from space in 1997 with the Midcourse Space Experiment (MSX) by Jenniskens *et al.* (2002), also showed what appeared to be the OH *A-X* band. However, these data were noisy, and there can be potentially large residuals arising from the imperfect subtraction of the background airglow in limb scanning observations. More convincing detections in spectra of meteors and their persistent trains were obtained from ground-based and airborne observations of near-UV spectra by Abe *et al.* (2002, 2003) during the 2001 Leonid meteor storms. The calculated and observed spectra show good agreement in the band head positions.

Here, we further investigate this OH emission by searching for the rovibrational transitions in the $X^2\Pi$ electronic ground state of OH at near-IR wavelengths in the 780–840 nm range accessible by charge coupled device (CCD) detectors. Astrophysical observations of these OH ($X^2\Pi$) Meinel bands (Meinel, 1950) were recently reviewed by Abrams *et al.* (1994). The $\nu = 0$ level of the OH $A^2\Sigma$ state is about 4 eV above the $\nu = 0$ level of the $X^2\Pi$ ground state (Fig. 1), a similar energy difference than for many metal atom transitions observed in meteor spectra.

If OH is thermally excited at T ~4,400 K, as are the metal atom and air plasma emissions (Jenniskens *et al.*, 2004a), or if the *A-X* OH emission is due to airglow-type chemistry, then the OH Meinel bands are expected to be as strong as the *A-X* transition at 310 nm (*e.g.*, Pungor and Cornides, 1969). On the other hand, if the excitation conditions favor low vibrational levels in the upper state, then the optical Meinel bands are expected to be suppressed.

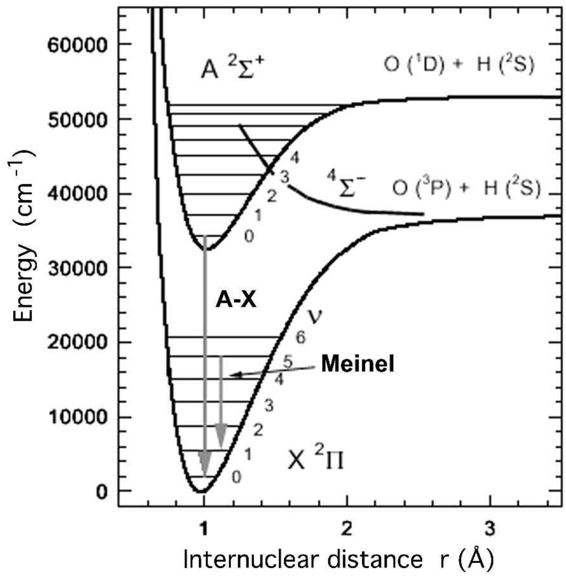

FIG. 1. Energy level diagram of OH with *A-X* (0,0) and Meinel band (5-1) transitions marked, after Luque *et al.* (1998).

METHODS

The meteor spectra from two bright Leonid meteor grains were obtained with a two-stage thermoelectrically cooled slit-less CCD spectrograph developed for this study. The instrument layout and response functions are discussed elsewhere in this issue (Jenniskens *et al.*, 2004a). In summary, a Pixelvision camera with two-stage thermoelectrically cooled 1,024 × 1,024 pixel back-illuminated SI003AB CCD with 24 × 24 μm pixel size and 24.5 × 24.5 mm image region was used in un-intensified mode. To decrease the readout time to below 1 s, spectra were recorded using 1 × 4 binning oriented perpendicular to the dispersion direction. The imaging optics was an AF-S Nikkor f2.8/300D IF-ED 300-mm telephoto lens, which provided a field of view of 5 × 5°. In front of the lens an 11 × 11 cm plane transmission grating #35-54-20-660 with aluminum coating was mounted on a 12-mm BK7 substrate by Richardson Grating Laboratory (Rochester, NY). We measured a groove density of 540 λ/mm and blaze wavelength of 698 nm (34°), which provided a full second order spectrum out to about 925 nm. No order filter was used, which resulted in overlapping third (and fourth) order spectra. The relative positions of the viewing direction and the meteor on the sky constrained the spectral range detected. Because of the small detector size, the wavelength scale was linear and matching to known lines in the spectrum provided the wavelength calibration. Any Doppler shifts from residual meteor motion were negligibly small and systematic.

RESULTS

The instrument was deployed over the continental United States onboard the U.S. Air Force 418th Flight Test Squadron-operated NKC-135 "FISTA" research aircraft during the 2001 Leonid Multi-Instrument Aircraft Campaign (Leonid MAC) at the time of the intense November 18, 2001, 10:40 universal time (UT) Leonid storm peak (Jenniskens and Russell, 2003). It was again deployed onboard NASA's DC-8 Airborne Laboratory on a mission from Spain to Nebraska during the 2002 Leonid MAC mission, during two storm peaks centered on 04:06 and 10:47 UT November 19 (Jenniskens, 2002). At the altitude of the observations, 37,000–39,000 ft, there was no detectable atmospheric water vapor absorption.

Detection of new molecular band

The first spectrum discussed here, we call "Homerun," was obtained at 10:44:58 UT, 2001 (Fig. 2), close to the peak of the 2001 meteor storm, which was due to an encounter with dust grains ejected by comet 55P/Tempel-Tuttle in 1767. The CCD frame shows the final part of the meteor trajectory in first order, which has a fairly flat light curve with a faint end flare. Based on the intensity of the 777 nm O I line, Homerun's visual brightness was estimated at -1 ± 1, which corresponded to a ~0.1 g meteoroid mass. In slitless mode, each emission line is an image of the meteor superposed on a background that consists of dark current and the light of stars accumulated during the full integration time of 0.4 s. A second exposure, taken within 2 s after the first spectrum (showing no residual emission), was subtracted from the original to remove the stars and background. All of the rows in the digital image were aligned and added into a single spectrum, which was calibrated for instrument vigneting and spectral response (Jenniskens *et al.*, 2004a). The spectrum covers a range of 137 nm from 708 to 845 nm in first order. There is second order overlap from the edge of the instrument's response curve (at about 370 nm) to the limit of the spectrum at 423 nm. Only strong lines were expected to be detected in third order because the instrument response is a factor of 100 less than in second order (Jenniskens *et al.*, 2004a).

As shown in Fig. 3, the resulting spectrum compares favorably with a spectrum calculated with NEQAIR2, which produced a model of air plasma radiation at the appropriate temperature and pressure (Laux, 1993, 2002). It is assumed in the model that the plasma is in local thermodynamic equilibrium (LTE), with the electron temperature the same as the heavy particle temperature. The modeled spectrum confirmed that the dominant emissions are from oxygen and nitrogen atoms and from the "first positive" *B-A* band system of molecular N_2 (Jenniskens *et al.*, 2004b).

The temperature of the emission plasma estimated from the NEQAIR2 models was particularly sensitive to the choice of emission ratios. The best fit to the overall shape of the N_2 first positive system (notably the slope at short wavelengths between 710 and 740 nm) indicates a vibrational temperature of 4,450 ± 50 K. Calculations using the ratio of intensities of the N I atom lines at 746 nm and the N_2 *B-A* emission intensity indicate a temperature of 4,430 ± 50 K. Chemical equilibrium of N I/N_2 occurs at a temperature of 4,380 ± 10 K. A comparison of the imaged and modeled spectra of the N I multiplet at 747 nm indicates that the calculated O I 777 nm lines (O I/N_2 matched for T ~4,310 K) is a factor of 2.5 times greater than the observed line. The

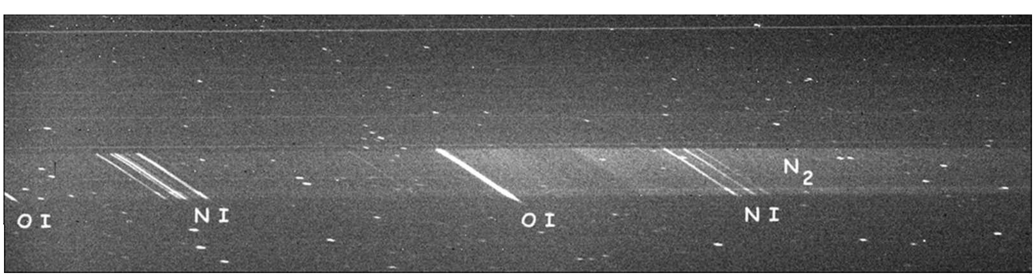

FIG. 2. First order spectrum of the 10:44:58 UT Leonid meteor ("Homerun") in the range 700–850 nm. The wavelength scale runs right to left. The meteor moved from top to bottom and ended during the exposure in a faint end flare. The main emission and telluric absorption lines and bands are identified.

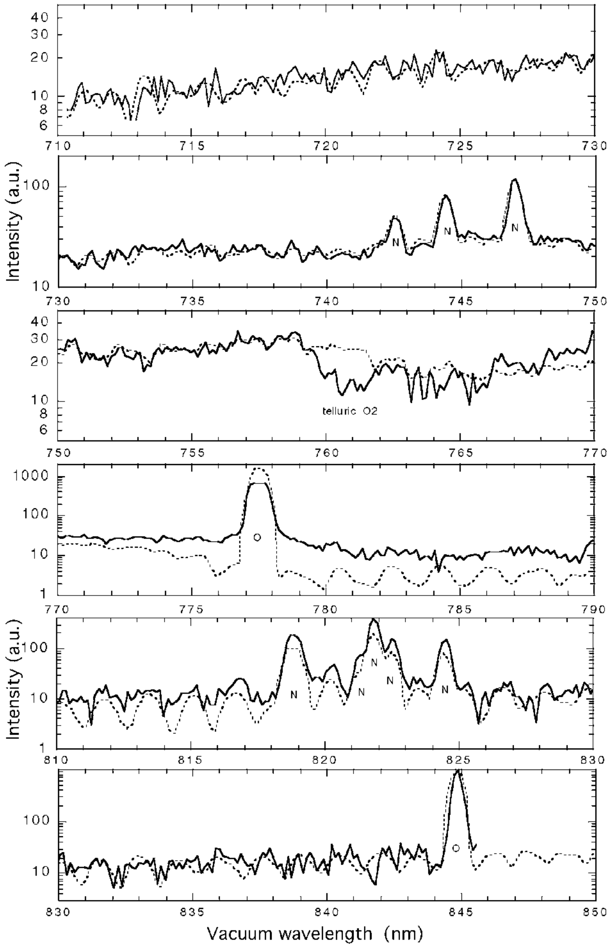

FIG. 3. Comparison of the 10:44:58 UT Leonid spectrum with an NEQAIR2 model of $T = 4{,}400$ K air plasma, representative for a pressure and air composition at 95 km altitude.

calculated N I multiplet at 822 nm (matched only at T = 4,475 ± 10 K) was found to be factor of 1.8 times fainter than the observed spectrum intensity. Calculations using the observed ratios of the O I line at 846 nm relative to the N_2 band indicate a temperature of 4,350 K. The intensity of the faint O I line at 799.7 nm is overestimated by a factor of about 2 in the calculated spectrum. These small discrepancies indicate small deviations from LTE (Jenniskens *et al.*, 2000a, 2004b).

To search for the OH Meinel band we subtracted the NEQAIR2 spectrum modeled for the N_2 and atomic line emission from the observed spectrum. Excess emission was observed for wavelengths between 770 nm and 840 nm (Fig. 4). The strong absorption peak at ~760 nm is due to telluric molecular oxygen, the column density of which is still significant at the altitude of the aircraft.

Within the region of excess emission are two emission maximums centered at about 789 and 815 nm. The blank spaces in the data correspond to the positions of the strong N I and O I lines. The spike at 777 nm is interpreted as a residual of the strong O I lines at that position (see below). The cause of the discrepancies between the observed and calculated spectrum are problematic, since laboratory spectra of the N_2 first positive system obtained by Laux (2002) are in excellent agreement with calculations performed with NEQAIR2.

Temporal evolution of the bands along the meteor track

Additional evidence indicating that the excess emission was not an artifact was obtained during the 2002 Leonid MAC mission. The second order spectrum between 767 and 849 nm of a very bright (−7 ± 1 magnitude) Leonid meteor was recorded at 09:21:26 UT (November 19), which we informally designated "Whow!," with third (511–566 nm) and fourth order (384–424 nm) lines overlapping (Fig. 5). The meteor was found to be 6.2 magnitudes (a factor of 300) brighter than "Homerun," based on the relative strength of the N I lines near 820 nm and the stronger molecular band emission. Nearly the complete meteor track was observed. The strong 777 nm O I line

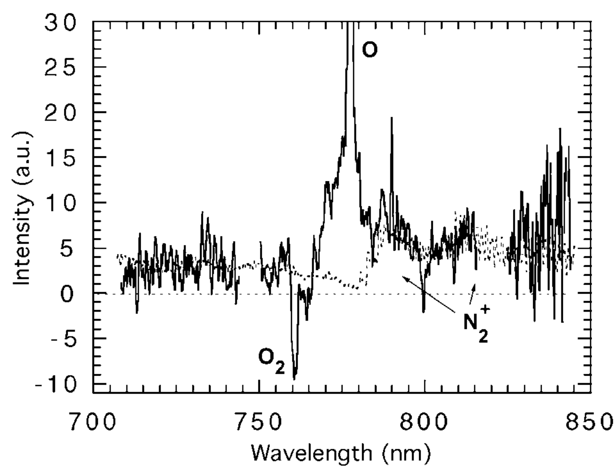

FIG. 4. Difference spectrum after subtraction of model air plasma emission bands of N_2 (first positive system) and lines of nitrogen and oxygen for the 10:44:58 UT Leonid. Two molecular bands and a residue of the O I 777-nm line remain, with a negative signal due to telluric absorption by the O_2 A (0,0) band. A dashed line shows an LTE NEQAIR2-modeled spectrum of the N_2^+ Meinel band.

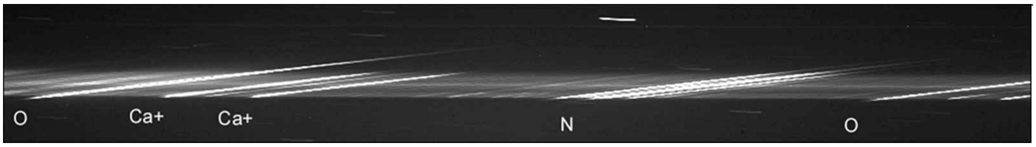

FIG. 5. The November 19, 2002, 09:21:26 UT Leonid meteor ("Whow!") was captured in a second order spectrum of the range 767–849 nm. The wavelength scale is left to right. The meteor moved from top to bottom. Second order air plasma emissions and fourth order meteoric metal atom lines of calcium ions are identified.

was already brightening when the exposure was started. Unlike "Homerun," this meteor track had no abrupt end: The second order O I and N I lines faded gradually after a broad emission flare. The onset of the flare was marked by a sudden onset of Ca^+ emission at 393.4 and 397.0 nm, observed in fourth order, a signature of fast and bright meteors (Harvey, 1971; Bronshten, 1983). Ca^+ emission is thought to arise from a different high temperature (~10,000 K) component rather than from other emission lines (Borovička, 1994). Again, an unexpected emission was observed after subtraction of the NEQAIR2 model for N_2 and atomic N I and O I lines in the range 780–820 nm, as well as the two maximum emissions centered at 789 and 815 nm. "Whow!," which was recorded in second order and at a different position on the CCD, corroborates the discovery of the new molecular band.

Figure 6 shows the temporal variation of the spectrum along the meteor trajectory by averaging subsequent samples of five rows in the spectrum. When the meteoroid penetrated deeper into the Earth's atmosphere, we saw that the N I/N_2 band ratio increased steadily. This indicates that the air plasma temperature increased slightly when the meteor penetrated deeper into the atmosphere, as discussed in Jenniskens *et al.* (2004b). When the N_2 band intensity dropped, the 815 nm band remained at the same intensity. This implies that the band is not directly related to the N_2 B-A $\Delta\nu = +1$ band series.

IDENTIFICATION OF THE NEW BANDS

Given that the 770–840 nm region in both spectra were nearly void of metal atom emissions, the excess emission cannot be attributed to a multitude of weak metal atom lines. The K I lines at 766.7 and 770.1 nm were detected in the 10:44:58 UT spectrum, but only at the 2 σ level (4 intensity units). No other emission lines from meteor metal atom ablation products were found to be present. The strongest anticipated (intrinsically faint) lines would have been those of Mg I (766.0 and 774.6 nm) and Fe I (832.6 and 838.7 nm).

The excess emission cannot be attributed to overlapping second-order molecular bands from the wavelength range between 370 and 423 nm. There are no strong molecular bands in this re-

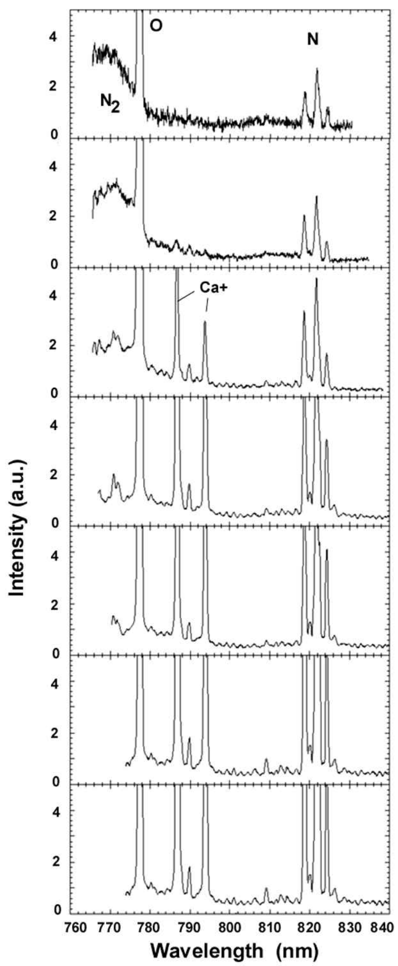

FIG. 6. Temporal evolution of the "Whow!" Leonid in a sequence of spectra averaged over five rows along the meteor path (top is beginning). Air plasma and meteoric metal atom lines of calcium are identified.

gion in similar Leonid meteors (Rairden *et al.*, 2000; Jenniskens *et al.*, 2004a) that were analyzed using an instrument with a sensitivity factor of 100 less than the instrument used in this study. Molecular band emission in first order provides the most likely explanation for the observed excesses at 789 and 815 nm.

The case for N_2^+

The new band is well matched with either the red (*A*-*X*) system of CN or the Meinel (*A*-*X*) system of the isoelectronic N_2^+. Figure 4 compares the NEQAIR2 spectrum calculated for the N_2^+ *A*-*X* system with the spectrum of "Homerun." The difference in the position of the band heads between the CN and N_2^+ bands is negligible. Although these band heads partly reflect emission from the strong 777 nm O I line, they lie to the right of the O line. In the UV region, the first negative system (*B*-*X*) of N_2^+ has its (0,0) band head at 391.4 nm, which is significantly different from the corresponding (0,0) band head of the violet system (*B*-*X*) of CN at 388.4 nm (Fig. 7). Elsewhere in this issue (Jenniskens *et al.*, 2004a), we demonstrate that the (0,0) band of CN *B*-*X* at 388.4 nm is not present in the spectrum of the "Endflare" Leonid 09:05:58 UT (November 18, 2001). On the other hand, Fig. 7 shows a feature at the anticipated position of the N_2^+ *B*-*X* (0,0) band with the correct width that does not appear to be due to metal atom lines. Therefore we propose that the feature observed in the near-IR spectra of "Homerun" and "Whow!" is more likely to represent the N_2^+ Meinel system rather than the CN red system.

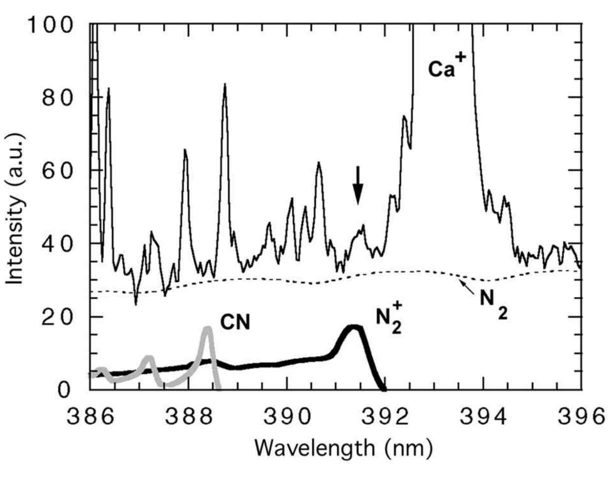

FIG. 7. A tentative identification of the first negative transition of N_2^+ (arrow) in the spectrum of the "Endflare" 09:05:58 UT (November 18, 2001) Leonid discussed in Jenniskens *et al.* (2004a). The N_2^+ band head is significantly displaced from that of isoelectronic CN.

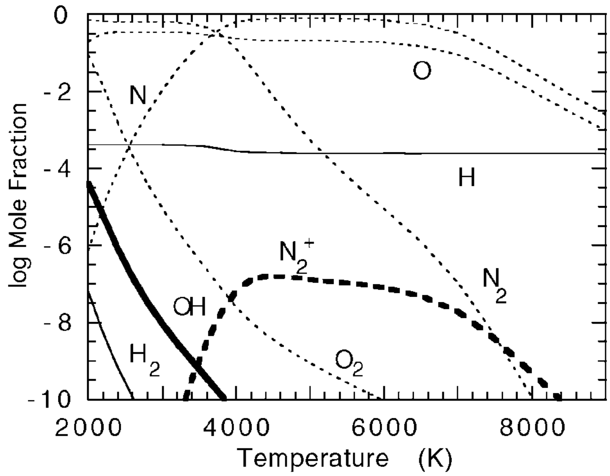

FIG. 8. Change of air plasma composition as a function of temperature from LTE calculations using STANJAN software (Reynolds, 2002) for a composition of 0.033% CO_2, 1% H_2O, and the pressure of air plasma at an altitude of 95 km.

This finding is the first detection of the N_2^+ molecule in bright meteors. The first negative system N_2^+ (1-) was tentatively detected by Mukhamednazarov and Smirnov (1977), who observed the weaker (0,1) band at 427.7 nm in the spectra of faint 3–5 magnitude meteors with the help of intensified TV cameras. However, that observation was never confirmed with modern techniques. The first negative bands were never found in bright (approximately –5 magnitude) meteors (Bronshten, 1983).

Implications

The N_2^+ first negative system is well studied in laboratory air plasmas (Laux *et al.*, 2001; Laux, 2002). Figure 8 shows the expected abundances in an LTE air plasma at 95 km altitude. At 4,400 K, the abundance ratio of $[N_2^+]/[N_2] = 5 \times 10^{-7}$. From the measured N_2^+/N_2 band intensity ratio of the "Endflare" 09:05:58 UT Leonid spectrum, we calculated an abundance ratio $[N_2^+]/[N_2] = 2 \times 10^{-9}$, which is over 2 orders of magnitude less than the expected LTE abundance. Thus the N_2^+ concentration is surprisingly weak in these meteor spectra.

If the red band in "Homerun" and "Whow!" is indeed N_2^+, then the $[N_2^+]/[N_2]$ abundance ratio for "Whow!" is a factor of 10 larger, though it is still less, by an order of magnitude, than the expected abundance ratio. The difference in the calculated N_2^+ abundance between the two meteors is not a significant argument against the N_2^+ identification (see below).

Bronshten (1983) pointed out that the low abundance could be the result of a higher than expected electron density: Although N_2^+ is formed by electron impact on N_2 molecules:

$$N_2 + e \rightarrow N_2^+ + 2e \quad (1)$$

N_2^+ is also destroyed by electrons:

$$N_2^+ + e \rightarrow N + N \quad (2)$$

Our abundance calculations do not support that explanation. The more likely excitation process is by atom or molecule rather than electron impact, because there are many more heavy species than electrons (both having the same energy since the plasma is close to LTE). We propose that the abundance is lower than expected because of the presence of meteoric metal atoms, which were not included in our calculations of plasma composition. As these meteoric metals have lower ionization potentials than N_2, we expect rapid (exothermic) charge transfer reactions in addition to charge transfer reactions with atmospheric species:

$$N_2^+ + Fe \rightarrow N_2 + Fe^+ \quad (3)$$

This can also account for the even lower N_2^+ abundance calculated for the "Endflare" Leonid, which displayed a metal atom line-rich spectrum. Unlike for meteors, the N_2^+ ion is a strong contributor to the glow of re-entry spacecraft, such as the Space Shuttle, at heights of 50–80 km where they are subjected to a 20,000–40,000 K hot and metal-atom-free shock (Viereck *et al.*, 1992; Park *et al.*, 1998; Mazzoufre *et al.*, 2002).

In addition to the N_2^+ band, there is excess of emission centered on the strong O I 777.4 nm line. This excess displays the shape of a Voigt line profile (Fig. 4). This emission is most likely due to scattered light in the spectrograph (after diffraction). We cannot exclude, however, the possibility that this emission is a yet unidentified molecular band unrelated to the N_2 first positive band. Laux (2002) detected a similar excess emission in laboratory measurements of air plasma.

THE SEARCH FOR OH MEINEL EMISSION

The new spectral feature attributed in the previous section to the N_2^+ (A-X) system cannot be due to water vapor emission because the $3\nu+\delta$ polyad water vapor band (clumps of overlapping vibrational bands) peaks at 820 nm, at the position of N I lines.

At the meteor plasma temperature of 4,400 K, water is effectively dissociated into H and OH, while OH is dissociated into O and H, given sufficient time. We calculated the expected mole fractions of OH in air plasma at various temperatures, assuming an air composition with 0.033% CO_2 and 1% H_2O at $P = 10^{-6}$ atm, representative for an altitude of 95 km (Fig. 8). At 4,400 K, we found OH abundances a factor of 10^5 times smaller than needed to account for the reported OH A-X emission (Abe *et al.*, 2002; Jenniskens *et al.*, 2002), even if the water content in the mesopause at ~90 km is as high as 20 ppm (Conway *et al.*, 1999; Stevens *et al.*, 2001). Hence, if OH is confirmed from its emission band at 310 nm to be present in the meteor plasma, it will signify non-equilibrium chemistry, for example, by release of water, hydrogen, or OH from meteoric minerals. If OH molecules are formed from a mineral water or organic precursor, then some molecules would survive for a period of time at 4,400 K, leading to a detectable signal. This is how such warm OH is detected in laboratory settings.

The anticipated OH Meinel band spectrum has many features due to the relatively large rotational constant of OH, which results in a wide band with well separated P, Q, and R branches (Herzberg, 1950). At first approximation, we assume that the vibrational distribution corresponds to the effective temperature of the meteor's air plasma (Jenniskens *et al.*, 2004b). The collision frequency at this altitude of the atmosphere is on the order of 10^4 s^{-1}, while the average lifetime of OH in the vibrational state (*e.g.*, 6 in the ground state) is on the order of 10^{-2}–10^{-3} s^{-1} (Turnbull and Lowe, 1989). Thus it is reliable that OH ($\nu = 6$) is in thermal equilibrium for the lower rotational states. In the particular wavelength range, it is the $\nu'' \rightarrow \nu' =$ 8-4, 8-3 (731–741 nm), 5-1, and 6-2 (831.2–874.5 nm) rovibrational bands with P, Q, and R branches from $\Delta J = 0, \pm1$ that contribute to the observed emissions. Each band has six main branches (Q1, Q2, R1, R2, P1, and P2). Each branch consists of a large number of rotational lines.

Figure 9 compares the observed spectrum with this calculated LTE spectrum of the OH Meinel bands. We found no correspondence between the strongest expected OH emissions in the (6,2) and (5,1) bands and features in our spectrum. We derived an upper limit of <10% for the integrated OH (5-1) Meinel band strength versus that of the 310 nm *A*-*X* band, by assuming that the noisy OH *A*-*X* signal in the MSX spectrum (Jenniskens *et al.*, 2002) relative to the N_2 first positive band at 760 nm was at the same intensity ratio as in our meteors. The N_2^+ band prevented us from setting an even stronger upper limit.

*The excitation of OH (*A-X*) in meteors*

Unfortunately, the lack of an OH Meinel band emission does not reveal any new insight regarding the presence of water in cometary minerals. The relative intensity of the *A*-*X* and Meinel band emission can vary strongly, depending on excitation conditions, and all of the more likely scenarios predict intense *A*-*X* emission.

The Meinel band dominates in the Earth's airglow, where excited OH is produced by the ozone–hydrogen mechanism (Bates and Nicolet, 1950; Herzberg, 1951; McKinley *et al.*, 1955):

$$H + O_3 \rightarrow OH\ (X^2\Pi,\ \nu = 0) + O_2 + 3.3\ \text{eV} \quad (4)$$

The exothermicity is sufficient to excite the OH molecules up to a vibrational level of $\nu' = 9$. As a result, the OH (9-4) band tends to be unusually strong between 770 and 790 nm (Chamberlain and Roesler, 1955). In a meteor plasma at $T \sim 4{,}400$ K, Reaction 4 can result from any source of hydrogen atoms reacting with ambient ozone molecules. However, such reactions are more likely to occur in a persistent train emission because hydrogen has to diffuse outward. The ozone abundance is expected to be very low in meteoric plasma (Jenniskens *et al.*, 2000b; Kruschwitz *et al.*, 2001).

The OH Meinel bands are relatively strong in hydrogen flames. The rate-limiting reaction in the combustion of hydrogen and hydrocarbons is the endothermic reaction (Yu *et al.*, 1994):

$$H + O_2 \rightarrow OH^*\ (X^2\Pi,\ \nu = 0) + O\ (^3P) - 0.7\ \text{eV} \quad (5)$$

which requires about 4.7 eV to form OH* ($A^2\Sigma$, $\nu = 0$). A plasma temperature of 4,400 K corresponds to a $kT = 0.38$ eV of translational energy, and any products from the high-energy tail of the distribution will primarily be in the lower ν level $X^2\Pi$ state, resulting in Meinel bands, but weak *A*-*X* emission.

At the other extreme, OH *A*-*X* emission is strong in combustion reactions with molecular oxygen in flames, where a significant fraction of OH molecules is formed in the low ν levels of the upper state (just below the dissociation limit, Fig. 1), because of the reaction (Walsh *et al.*, 1998; Luque *et al.*, 1998; Abid *et al.*, 1999):

$$\text{—CH} + O_2 \rightarrow \text{—CO} + OH^*\ (A^2\Sigma,\ \nu = 0) + <2.9\ \text{eV} \quad (6)$$

A significant fraction of that excess energy goes into translational motion. Only if OH* ($A^2\Sigma$) is formed in excited vibrational states with $\nu > 5$, which requires a $kT > 1.6$ eV of translational energy, will there be strong Meinel band emission in the wavelength range studied here.

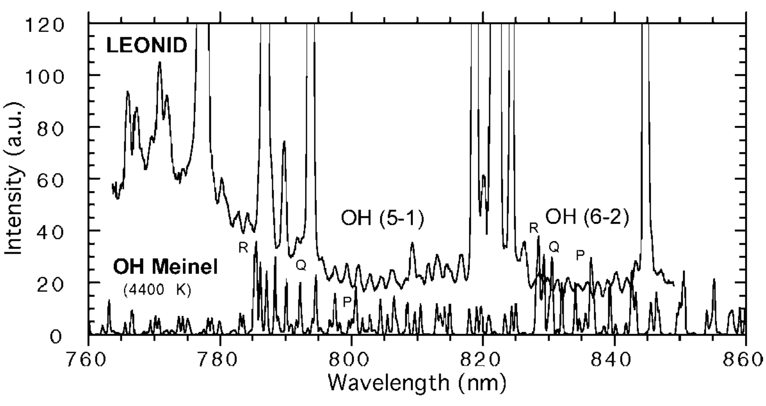

FIG. 9. Search for OH Meinel band emission in the spectrum of the "Whow!" Leonid. The NEQAIR2 model is for T = 4,400 K and pressure and composition representative for an LTE air plasma at an altitude of 95 km.

The most likely mechanism for strong OH *A-X* emission is the dissociation of water by UV or x-ray photons, and by electrons. Photons with wavelengths less than 190 nm can drive this reaction (at UV wavelengths above 190 nm and into the visible wavelength range, water is not very absorbent). In meteor plasma, strong UV emission has been observed from N I and O I lines at 114–136 nm (Carbary *et al.,* 2003). Any atmospheric water vapor or mineral water will be dissociated by these UV photons predominantly in the second absorption band according to (Crovisier, 1989):

$$H_2O + h\nu \rightarrow OH^* (X^2\Pi, \nu = 0) + H + \sim 3.1 \text{ eV} \quad (7)$$

with a ($\nu = 0$) branching ratio of ~0.8. About 10% of OH is produced in the excited *A* state, resulting in *A-X* emission. In this reaction, the hydrogen atom carries most of the excess translational energy (at 1.85 eV per dissociation). Due to momentum conservation, translational speeds for OH and H are about 1.01 and 17 km/s, respectively. The mean energy available for vibrational and rotational excitation is about 1.29 eV per dissociation. This is not enough to populate the high ν levels significantly, and only very weak Meinel band emission is expected. On the other hand, if this mechanism is important, then we might also expect some O (^{1}D) emission at 630 nm from the UV dissociation of OH, which has not been reported in meteor spectra.

Along similar lines, electron impact of water tends to form ground-state OH (Harb *et al.,* 2001). Significant populations of vibrationally excited states can result from the excitation of core electrons in water by x-rays, which leads to vibrationally excited OH* and neutral hydrogen (Hjelte *et al.,* 2001). It is unknown if x-rays are produced in meteor excitation.

CONCLUSIONS

A new molecular band was detected in the region from 780 to 820 nm, identified as the N_2^+ ion, though it was determined that the abundance of the ion is an order of magnitude less than expected for an LTE plasma. We hypothesize that charge transfer reactions with meteoric metal atoms are the likely cause of the low abundance of N_2^+, rather than the recombination of N_2^+ with electrons as was previously proposed.

From the lack of OH Meinel band emission, we conclude that the OH *A-X* emission in meteor spectra is not due to thermal excitation of OH molecules in the meteor plasma. Possible mechanisms to form excited OH* $A^2\Sigma$ at low vibrational levels are the UV dissociation of (atmospheric or meteoric) water molecules or the combustion of organic matter in the meteoroids.

To determine whether large cometary grains contain mineral water or trapped water in any form, it is necessary to confirm the presence of OH *A-X* emission and understand its excitation mechanism. Analysis of the OH *A-X* band profile as a function of meteor altitude in future high-resolution measurements may help decide which excitation mechanism is at work. The detection of O (^{1}D) emission from the UV dissociation of OH may also shed light on this issue. Finally, Fig. 8 suggests that "following the water" via influx of large cometary meteoroids implies searching for hydrogen atom emission in meteors.

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ABBREVIATIONS

CCD, charge coupled device; IR, infrared; LTE, local thermodynamic equilibrium; MAC, Multi-Instrument Aircraft Campaign; MSX, Midcourse Space Experiment; UT, universal time; UV, ultraviolet.

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