

N_2^+ and CO^+ in Comets 122P/1995 S1 (deVico) and C/1995 O1
(Hale-Bopp)

Anita L. Cochran, William D. Cochran and Edwin S. Barker
McDonald Observatory
University of Texas at Austin

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Abstract

We observed comets 122P/1995 S1 (deVico) and C/1995 O1 (Hale-Bopp) with high spectral resolving power in order to determine the ratio of N_2^+/CO^+ in their comae. While we clearly detected the CO^+ in both of these comets, no N_2^+ was detected in either comet. From these spectra, we derive sensitive upper limits for N_2^+/CO^+ . These upper limits are substantially below other reported detections of N_2^+/CO^+ in other comets. We discuss the prior N_2^+ detections and compare them with our observations. The abundance of N_2 in comets is important to our understanding of the condensation of ices in the solar nebula. In addition, N_2 is a tracer of Ar so study of N_2 allows an understanding of the role of comets for delivering volatiles to the terrestrial planets. It appears that many, if not most, comets are depleted in N_2 and it will be necessary to search for a mechanism for depleting this molecule in order to be consistent with current models of the solar nebula.

Introduction

Nitrogen is one of the more abundant elements in the universe and is therefore assumed to be an important constituent of the solar nebula and of the comets. Nitrogen probably exists in comets in the form of N_2 and other nitrogen-bearing molecules, including NH_3 . Indeed, the ratio N_2/NH_3 is a sensitive indicator of conditions in the solar nebula. Lewis and Prinn (1980) point out that at high temperatures and low pressures the dominant equilibrium species of carbon, oxygen and nitrogen would be N_2 , CO , and H_2O . Only as temperature and pressure regimes change will CH_4 and NH_3 be produced and N_2 and CO be depleted. They conclude that the conversion of N_2 to NH_3 and CO to CH_4 would be sufficiently slow relative to radial mixing in the primitive solar nebula so that only small amounts of NH_3 and CH_4 should be present. Conditions in the circumplanetary nebulae would be sufficiently different so that jovian planets might have increased NH_3 and CH_4 abundances (Prinn and Fegley 1981).

Comets delivered some of the volatiles that we see today in the atmospheres of the terrestrial planets, but it is not certain how important a source of volatiles the comets represent. Owen and Bar-Nun (1995a,b) have pointed out that N_2 is an important guide to the volatile abundances of comets because it is trapped and released by amorphous ice in a manner which is similar to argon (Bar-Nun *et al.* 1988). Using N_2 as a guide to the argon, one can determine the extent to which comets enriched the volatile and noble gas components of the terrestrial planets. Ices formed at low temperatures will trap gas from the surrounding nebula, fractionating the original mixture as a function of the local temperature. Thus, they suggest that comets which formed near Uranus and Neptune, at temperatures around 50 K, would be the source of noble gases for Earth and Mars, while the higher quantities of neon and argon in the atmosphere of Venus, compared with Earth, would require comets formed at colder temperatures, such as in the Kuiper belt, to be the deliverers of some of the volatiles.

We detect such species as NH , NH_2 and CN in every comet, so evidence of nitrogen carriers is easily available. Most of these species and their parents are chemically reactive in the comae of comets. Molecular nitrogen should be less reactive than species such as NH_3 or HCN . While spacecraft have flown past comet Halley with mass spectrometers onboard, measurement of N_2 is difficult with mass spectrometry since both N_2 and CO occupy the mass 28 bin of these instruments (cf. Everhardt *et al.* 1987 for a discussion of CO and N_2 from Giotto observations of Halley). Thus, disentangling the quantity of N_2 from the CO is very model dependent.

This leaves the field of ground-based spectroscopy for determining the quantity of molecular nitrogen. Ground-based studies of molecular nitrogen are very difficult, however, because of the N_2 abundance of the Earth's atmosphere. To circumvent the difficulty in observing N_2 , past observations have concentrated on the N_2 ion, primarily through observations of the N_2^+ (0,0) band at 3914Å. This band is extremely weak and is expected to be seen only in the tails of comets. Care must be taken when observing this band since N_2^+ emission is also excited in the atmosphere of the Earth, especially

near dusk and dawn, when comets are often observed. Auroral activity will also excite this band in the terrestrial atmosphere. Additionally, this weak feature can easily be confused with other, nearby, cometary emissions. Thus, accurate measurement of N_2^+ in cometary spectra requires both good spatial and spectral resolution to separate the features from that of the Earth and other cometary features.

Observations

We observed comets deVico and Hale-Bopp with the 2DCoude spectrograph (Tull *et al.* 1995) on the 2.7-m Harlan J. Smith telescope of McDonald Observatory. The 2DCoude has two operating modes. The “lower” resolution mode has a resolving power, $R=60,000$. In this mode, spectral coverage is complete from around 3800-5800Å and coverage continues to 1 μm with increasing interorder gaps. Typically, 60–65 spectral orders are observed. Therefore, in the blue, many molecular bands can be observed simultaneously, regardless of the exact grating setting. In the “high” resolution mode, $R=200,000$, but the coverage is much less complete than the lower resolution mode. Typically, high resolution covers 10–15 orders of approximately 15Å each. Thus, care must be taken to center key features on a spectral order and many features remain unobserved.

For this project, we observed comet Hale-Bopp in the high resolution mode, carefully centering the portion of the order containing the N_2^+ band on the CCD, while also observing the CO^+ (2,0) and (3,0) bands on two other orders. Since the CH^+ (0,0) band occurs at a wavelength coincident with the CO^+ (2,0) band, this ion was also observed. Comet deVico was observed in the lower resolution mode and the same three ions were observed. Table I gives the circumstances of the observations. For all observations, the slit was 8.2 arcsec long. For the Hale-Bopp observations, the slit was 0.34 arcsec wide, while it was 1.2 arcsec wide for deVico. Each slit width projects to two pixels on the CCD for the resolving power of the observations. Different positions within the coma were observed by moving the telescope around the sky under accurate computer control.

The data were reduced using the ECHELLE package of IRAF. Incandescent lamp observations were used to determine the flat field; ThAr lamp observations were used for calculating the dispersion curve. The rms errors of our fits for the dispersion curve are 0.24 mÅ for the Hale-Bopp spectra and 2.5 mÅ for the lower resolution deVico spectra. The solar spectrum was observed with an identical instrumental setup to that used for the comets by imaging the Sun through a diffuser on the roof of the spectrograph slit room and projecting this image through the slit in the same manner as objects observed through the telescope. Thus, we used an *observed* solar spectrum in our reductions.

Care was taken to preserve the relative flux levels of the spectra. The spectral orders were extracted by first tracing the order along the chip and carefully setting the edges of the apertures. Since the continua of the cometary spectra were rarely of high enough signal/noise to define well the aperture boundaries, it was assumed that the flat lamp boundaries were appropriate for the comet and only the position on the chip of

the center of the order was computed for the cometary spectra. Extraction was done using variance weighting. We used a 1D fit for stars and solar spectra, while a 2D fit was used for cometary spectra (because of the emission line nature of the cometary spectra). At the end of the routine reduction, we had files containing n spectra for each initial spectral image, where n is the number of extracted orders in the image (60 for deVico and 13 for Hale-Bopp).

The solar spectrum observations were used to remove the underlying continuum from the cometary spectra. Comet deVico has very little solar continuum, but the continuum of Hale-Bopp was quite strong. We corrected the comet and the solar spectrum for the geocentric and heliocentric Doppler shifts so that both were on a common rest frame. Then, the solar spectrum was carefully weighted to match the continuum level of the comet in regions away from cometary emissions. Some scattered light might still remain, but the amount is minimal and was removed when the line intensities were calculated.

Figure 1 shows the spectral order of the CO^+ (2,0) and the CH^+ (0,0) bands in the spectrum obtained 100 arcsec tailward of the optocenter of Hale-Bopp. For both these ions, the predicted molecular transitions in the spectrum are marked. Inspection of this figure shows that only very low J -levels are observed for CH^+ , while slightly higher J -levels are observed for CO^+ . However, even for CO^+ , J -levels above 10 or 11 are not seen.

Figure 2 shows the same spectral region for observations 100 arcsec tailward of the optocenter of comet deVico. The spectral coverage of an order is longer at the lower resolving power of the deVico observations. Even with this larger coverage, only one of the CO^+ (2,0) ladders is seen in these observations. Both CH^+ and CO^+ are again present, though the ratio of CH^+/CO^+ may be slightly different in these two comets.

Figure 3 shows the Hale-Bopp spectrum obtained 10 arcsec tailward of the optocenter in the spectral order which should contain the N_2^+ (0,0) band. The N_2^+ transition is a $\text{B}^2\Sigma-\text{X}^2\Sigma$ transition and therefore does not have a Q-branch. The P- and R-branch line positions marked are from Dick *et al.* (1978) and have an accuracy of $0.01 \text{ cm}^{-1} = 2 \text{ m}\text{\AA}$. Although the solar-subtracted spectrum is somewhat noisy, there are no believable features. There might be a spike at 3909\AA and a broader spike at 3913.5\AA . Neither of these is coincident with any of the N_2^+ line positions. The errors in the wavelengths of our spectra, coupled with the N_2^+ laboratory errors would lead us to expect coincidence to $2 \text{ m}\text{\AA}$. The most believable feature is the broad feature starting at 3914.5\AA and degrading redward. The positions of the C_3 (0,2,0)-(0,0,0) band transitions are marked underneath the spectrum. The feature seems to match well the R-branch bandhead of this C_3 band. Thus, we conclude that if the feature is real, it is some residual C_3 emission. Since this spectrum was obtained only 10,000 km from the optocenter, this does not seem an unlikely species to observe. Inspection of the spectrum obtained 100 arcsec tailward of the optocenter shows even less evidence for features. We therefore conclude that we did not detect *any* N_2^+ in the spectrum of Hale-Bopp.

Figure 4 shows the comparable spectral region for comet deVico, 100 arcsec from the optocenter. There appears to be an upward fluctuation between 3913.5 and 3915.1Å, with spikes at 3913.9 and 3914.9Å. However, at R=60,000, it is impossible to tell if this feature is a molecular band and, if so, which way it degrades, or to differentiate whether it is C₃ or N₂⁺. The N₂⁺ P-branch bandhead occurs at 3914.3Å and distinct lines of the P-branch should be visible. We do not detect lines at the expected wavelengths, within the 3 mÅ wavelength uncertainties. On the strength of the Hale-Bopp observation, this feature could be C₃. With the larger spectral coverage of the R=60,000 orders, the blue end of this order contains the CN (0,0) bandhead (not shown in Fig. 4). Thus, we were able to use the high signal/noise CN emission lines to confirm that there were no errors in our wavelength solution or in our Doppler shift corrections. The centers of the CN lines fell at the correct wavelengths, verifying that any spikes in the N₂⁺ region would also have to be at predicted wavelengths.

For the deVico observations, our only spectrum off the optocenter was obtained more than 70,000 km into the tail. Thus, it is reasonable to ask about the likelihood that we observed C₃ this far from the optocenter. Figure 5 shows the optocenter spectrum from the same night. We show more of the order to illustrate the abundance of molecular emissions observed. The CH B-X (0,0) band is clearly detected along with several C₃ bands. Indeed, inspection of this plot shows there are several broad, unidentified features whose structure seems similar to the identified C₃ bands. Thus, it is likely that this order is riddled with C₃. However, comparison of the strength of the strongest C₃ band, the (0,0,0) – (0,0,0) band, in the optocenter and tail spectra makes it unlikely that we detected the much weaker (0,2,0) – (0,0,0) R-branch bandhead in the tail spectrum. Thus, it is most likely we detected only noise in the deVico spectrum.

In summary, we do not believe that any N₂⁺ was detected in the spectra of comets Hale-Bopp or deVico. The CO⁺ and CH⁺ were clearly detected in both comet’s spectra. We are therefore able to place limits on the important ratio of N₂⁺/CO⁺ in these two comets.

Limits on N₂⁺/CO⁺

For both comets Hale-Bopp and deVico, the CO⁺ (2,0) band was clearly detected. Thus, we can derive an abundance of CO⁺ from these data for comparison with other comets. However, coudé data can not be easily calibrated into absolute fluxes, so we must work with band intensities in detector counts. In addition, typical lower resolving power observations observe all branches of the CO⁺ band, while we only observe the ²Π_{1/2}(F₂) branches. We took the simple approach of “integrating” the band by fitting a continuum and summing the counts in the band above the continuum. We limited our bandpass to just the region of the detected lines. These values are given in Table II. While a larger bandpass would be more comparable to prior low-resolution observations of comets, it is inappropriate for high resolution observations since larger bandpasses would increase the noise with no increase in signal. Typical low-resolution observations do not return

to continuum in between the lines of different bands.

We do not believe that we have detected the N_2^+ in either comet. We computed upper limits by computing how much of a band could be hidden within the noise. We did this by computing the rms in a bandpass. Then, the upper limit is just $1/2 \times \text{rms} \times \text{bandpass}$, in appropriate units. These are 2σ upper limits. For the same rms, more signal can be hidden in a large bandpass than a small bandpass. Since we do not know exactly how many lines would be likely to be detected, we cannot easily define the bandpass. We assumed a bandpass which would include the complete P-branch of N_2^+ . The derived counts, which are 2σ upper limits for what could be hidden in the noise, are listed in Table II, column 3.

With the use of a few assumptions and simplifications, we can use our values to derive N_2^+/CO^+ for these two comets. Examination of the solar spectra in these two regions, in comparison with the published atlas of Kurucz *et al.* (1984), shows that the sensitivity of the N_2^+ order is lower than that of the CO^+ order. To match their sensitivity, we would need to multiply the N_2^+ upper limits by a factor of 1.7. However, the calibration of the solar spectrum depends on details such as activity, so this factor is uncertain. We do have observations of α Lyr with the same instrumental setup as for deVico, but since the N_2^+ band occurs in the Balmer decrement, where the α Lyr flux changes rapidly with wavelength, the α Lyr flux is not calibrated in this region. Assuming a smooth decrease through the Balmer decrement, we confirm that a correction factor of 1.5–1.7 for the N_2^+ counts would be appropriate. We therefore adopt a factor of 1.6.

Once the band intensity is known, the column density can be computed using

$$N = L/g_{\nu'\nu''}$$

where N is the column density, L is the integrated band intensity and $g_{\nu'\nu''}$ is the excitation factor. We used excitation factors of 7.0×10^{-2} photons $\text{sec}^{-1} \text{mol}^{-1}$ for the N_2^+ (0,0) band (Lutz *et al.* 1993) and 3.55×10^{-3} photons $\text{sec}^{-1} \text{mol}^{-1}$ for the CO^+ (2,0) band (the average value from Figure 2 of Magnani and A'Hearn 1986). Then,

$$\frac{N_2^+}{\text{CO}^+} = \frac{g_{\text{CO}^+}}{g_{N_2^+}} \frac{L_{N_2^+}}{L_{\text{CO}^+}}$$

For CO^+ , we observed only one of the two ladders. If we assume the two ladders are equal strength, we should multiply our CO^+ intensity by two for the calculation. We likewise need to multiply the N_2^+ upper limits by a factor of two since we have only measured the P-branch and the R-branch should have a similar intensity. In Table II, column 4, we list our upper limits for N_2^+/CO^+ , including using a factor of 1.6 to correct for the sensitivity difference of the two orders.

It would be impossible to hide much N_2^+ in our spectra. Figure 6 (upper panel) shows one of the Hale-Bopp spectra, as observed, and, in the lower panel, the same

spectrum with a feature added which has enough integrated counts to yield the Halley N_2^+/CO^+ ratio (Wyckoff and Theobald 1989 – discussed below). We do not claim that this synthetic band is the exact shape that would be present, nor are the “lines” at exactly the N_2^+ wavelengths, but it gives an idea of the ease with which we would detect such a feature. Clearly, no feature this distinctive could be missed in our observations.

Previous Observations of N_2^+

Most comets are not bright enough to be observed with the high spectral resolving powers that we used for deVico and Hale-Bopp. This was especially true in the past, when detectors, such as photographic plates, had much lower quantum efficiency than our current CCD detectors. Therefore, prior observations which have detected N_2^+ in cometary spectra have been obtained with lower resolution, often on photographic plates.

The N_2^+ feature is generally weak and is overwhelmed by other molecular emissions near the optocenter. In addition, since N_2^+ is an ion, it is entrained in the solar wind magnetic field and rapidly accelerated into the tail. Thus, spectra of the tail region are necessary for its definitive detection, yet tail spectra are generally of lower signal/noise than near-optocenter spectra since the cometary brightness falls with increasing cometocentric distance. Despite these difficulties, observations of comets exist which show the detection of N_2^+ in the tails of comets.

Only two of the prior reported observations are digitally measured spectra; the rest are estimates from digital spectra or are photographic spectra. Wyckoff and Theobald (1989) report a detection of N_2^+ in the tail of comet Halley at a cometocentric distance of 3×10^5 km tailward. These observations were at much lower resolution than our observations. They detected a weak emission in the region from 3885–3950Å which they concluded was composed of contributions from the CO^+ (5,1), CO_2^+ (unassigned), N_2^+ (0,0) bands and an unidentified band. By modeling the combined feature, they were able to estimate the contribution of N_2^+ to the mixture. Using this estimate and the average for the CO^+ (2,0), (3,0) and (4,0) column densities, they derived a value of $\text{N}_2^+/\text{CO}^+ = 0.004$. However, the excitation factor which Wyckoff and Theobald used for N_2^+ was not accurate and Wyckoff *et al.* (1991b) revised the value of the column density of N_2^+ using the excitation factors of Lutz (1989—a personal communication). This excitation factor is the same as that given in Lutz *et al.* (1993). If we apply the value from Lutz *et al.*, then $\text{N}_2^+/\text{CO}^+ = 0.002$. If only the (2,0) band column density of CO^+ is used, then $\text{N}_2^+/\text{CO}^+ = 0.003$.

Lutz *et al.* (1993) reported observations of the tails of two comets obtained at low resolution ($\sim 10\text{Å}$). For comet Halley, they obtained spectra at 2×10^4 and 2×10^5 km from the optocenter in the tailward direction. They claim to have detected no N_2^+ emissions in the Halley tail spectra. However, they also did not detect the CO^+ emissions in several Halley spectra. Their derived upper limits for N_2^+/CO^+ when CO^+ was detected were higher than the Wyckoff and Theobald detection.

In addition to observations of Halley, Lutz *et al.* also observed comet C/1987 P1 (Bradfield=1987 XXIX). For this comet, spectra were obtained at 2×10^4 and 6×10^4 km from the optocenter. CO^+ was detected in both spectra, but N_2^+ was only detected at the larger cometocentric distance. At their resolution, the N_2^+ feature is on the wing of the CN (0,0) band. No mention is made of the possible contamination of this feature by the CO^+ (5,1) band. Assuming all of their measured band was N_2^+ , Lutz *et al.* derive a value of $\text{N}_2^+/\text{CO}^+ = 0.02$.

The vast majority of observations of cometary tails were photographic. Not only were they at lower resolving powers than our observations of deVico and Hale-Bopp, but photographic plates are even more difficult to calibrate! Non-uniformity in response and vignetting of the spectrograph slit cause difficulty interpreting these spectra. Still, there are many fine examples of photographic spectra and these can be used to determine the N_2^+/CO^+ ratio for some comets. The largest published collection of photographic spectra is that of Swings and Haser (1956). Examination of the plates in this atlas shows some comets for which CO^+ and N_2^+ are both apparent, while other comets show evidence of tails (i.e. CO^+) but no N_2^+ . Arpigny examined these and other photographic and digital spectra at his disposal and estimated the intensity ratio for the N_2^+/CO^+ , where the CO^+ band used was the (4,0) band because of its proximity to the N_2^+ emission (1999, personal communication). Table III lists the 12 comets which he determined had both N_2^+ and CO^+ in these spectra, along with his estimate of the ratio of the intensity of the two bands (column 2). In order to compare his intensity ratios with other observer's column density ratios, it is necessary to multiply by the ratio of the excitation factors, as before. Since the (2,0) CO^+ was used in our work and in other published ratios, we converted the intensity ratios in Table III by using the relationship $I(4, 0) = 0.6 \times I(2, 0)$, where $I(4, 0)$ is the intensity of the (4,0) band, $I(2, 0)$ is the intensity of the (2,0) band, and the factor is taken from Table 4 of Magnani and A'Hearn (1986). The resultant column density ratios are given in column 3 of Table III. Arpigny's estimates of the intensity ratios are consistent with the published numbers for comet Bester (Swings and Page 1950) and comet Humason (Greenstein 1962). It should be noted that Warner and Harding (1963) also observed comet Humason at a comparable heliocentric distance (however they only discuss CO^+ , not N_2^+). However, it is clear from Arpigny's compilation that N_2^+ has been observed in previous spectra of some comets.

In addition, Arpigny reported four comets which had good spectra but for which no, or only very faint, evidence of a plasma tail existed. These comets are C/1948 V1 (Eclipse), C/1963 A1 (Ikeya), C/1968 N1 (Honda), and C/1975 N1 (Kobayashi-Berger-Milon). Arpigny points out that N_2^+ emission is always very weak, so we should not expect to see it when the CO^+ is weak or non-existent.

Our own examination of the atlas of Swings and Haser (1956) found five comets for which there was evidence of a tail but no evidence for N_2^+ . The Big Comet of 1910 (1910 I) showed only continuum in the tail, so this was presumably a dust tail. Comets Halley (1910 II), Brooks (1911 V), Gale (1912 II), and Jurlof-Achmarof-Hassel (1939 III) showed evidence of weak CO^+ emission but no N_2^+ emission (Arpigny notes that N_2^+ was observed by Bobrovnikoff in spectra of Halley obtained in 1910, but these spectra are

not included in the Swings and Haser Atlas). These would be similar to Hale-Bopp and deVico in the absence of N_2^+ while other ions are present. However, with the weakness of the CO^+ emissions in these four photographically observed comets, the N_2^+ emission is most probably below the plate sensitivity.

Implications

In this paper, we have presented high resolution observations of two comets with which we were able to study the relative abundances of N_2^+ and CO^+ . These two ions are proxies for understanding the quantity of N_2 and CO , two of the least chemically reactive cometary coma species. Conversion from the quantity of the ions to the quantity of the neutrals is dependent on an understanding of the photodestruction branching ratios which are not well understood (Wyckoff and Theobald argue you must multiply the ion ratio by a factor of 2, while Lutz *et al.* find no factor necessary), so we will continue to discuss these species in terms of their ions. For both Hale-Bopp and deVico, CO^+ was easily detected but N_2^+ appears to be missing from the spectra. Thus, we have put very low upper limits on the ratio of N_2^+/CO^+ . We note, however, that there are previous observations of comets which show CO^+ but not N_2^+ for which sensitive upper limits cannot be derived.

The quantity of N_2 and CO expected in a comet depends on several factors including the temperature at which the ice was deposited, when in the history of the formation of the solar system the gases were trapped in the ice and the orbital history of the comet itself. Current models of the solar nebula have comets which now reside in the Oort cloud forming in the Uranus-Neptune region (cf. Weissman 1991; Duncan, Quinn and Tremaine 1987). The temperature in this region was probably about 50 ± 20 K (Boss *et al.* 1989). Thus, a first guess to the deposition temperature of cometary ices is 50K. This is consistent with laboratory experiments described by Owen and Bar-Nun (1995b).

The first direct measure of a deposition temperature for ice came with observations of deuterium in comet Hale-Bopp. Meier *et al.* (1998b) reported the detection of HDO in Hale-Bopp and determined a ratio of $\text{D}/\text{H}=(3.3 \pm 0.8) \times 10^{-4}$ in H_2O . In addition, Meier *et al.* (1998a) detected DCN for the first time and derived a ratio of $\text{D}/\text{H}=(2.3 \pm 0.4) \times 10^{-3}$ in HCN . Note that the D/H ratio is different for these two species, with D/H measured from HCN 7 times higher than from H_2O . Since the D/H enrichment for different molecules is a strong function of temperature, Meier *et al.* (1998a) were able to derive a temperature for the cloud fragment in which this comet formed of *no colder than* 30 ± 10 K.

Bar-Nun *et al.* (1988) performed laboratory experiments on deposition of various gases along with H_2O ice and showed that CO is trapped 20 times more efficiently than N_2 in amorphous ice which formed at 50K, when these two gases are present in equal abundances with CH_4 and Ar . This ratio changes slightly when only CO and N_2 are present in the gas (Notesco and Bar-Nun 1996, Table I) but generally shows enrichment factors of 15–30. From these laboratory experiments, Owen and Bar-Nun

(1995a) concluded that icy planetesimals formed in the solar nebula at around 50 K, the temperature at which the studied comets should have formed, would have $N_2/CO \approx 0.06$ in the gases trapped in the ice if $N_2/CO \approx 1$ in the nebula. The predicted cometary ratio of N_2/CO is much higher than our upper limits for deVico and Hale-Bopp and is higher even than the detections of Wyckoff and Theobald (1989) and Lutz *et al.* (1993), though some of the estimates might show ratios this high.

Several factors might mitigate this discrepancy. Prialnik and Bar-Nun (1990) point out that the gas/water vapor ratio is not necessarily representative of the ratio of ices in the nucleus. However, the laboratory experiments of Bar-Nun *et al.* (1988) have demonstrated that CO and N_2 should be released simultaneously in the same proportion as they exist in the ices. There is evidence for a source of CO at around 10,000 km from the nucleus (Eberhardt *et al.* 1987) which may be attributable to grains. In addition, Krankowsky (1991) points out that H_2CO is probably an additional parent for CO. Thus, there may be additional mechanisms for the production of CO which do not exist for N_2 . While these factors might change the predicted ratio for N_2/CO , Owen and Bar-Nun (1995a) go on to make the specific prediction that “future observations of dynamically new comets will show values of N_2/CO systematically higher than those in well-established short-period comets”. They point out that as comets are continuously exposed to solar radiation in the inner solar system, they would be expected to lose any N_2 in their outer layers in a brief period of time.

Figure 7 shows all of the values and limits discussed in this paper, plotted as a function of $1/a_o$, the original semimajor axis [four of the values for the estimates are the oscillating $1/a$, as noted in Table III; for C/1987 P1 (Bradfield) $1/a_o = 0.006380$ (Marsden and Williams 1995); for Hale-Bopp $1/a_o = 0.00535$ and for deVico $1/a_{osc} = 0.057$ (Marsden personal communications 1999)]. For the Wyckoff and Theobald Halley observation, we include the range of derived values.

If one ignores the Hale-Bopp upper limit, there would seem to be an increase of N_2^+/CO^+ with decreasing $1/a_o$, as was predicted by Owen and Bar-Nun. However, the trend is based mostly on Arpigny’s estimates, which are approximate. In addition, the Hale-Bopp upper limit can not be discarded since it is clear from inspection of the spectrum in Figure 6 that even as much N_2^+ as would be needed to equal the Halley N_2^+/CO^+ cannot be hidden in this spectrum. Conversely, while the values for the ratio can be questioned for the estimates, inspection of the atlas of Swings and Haser (1956) and spectra such as the Humason spectrum of Greenstein (1962) clearly show an emission which is coincident with the location of the N_2^+ feature. Thus, at least some comets have some N_2^+ in their spectra. However, at lower spectral resolution, blending of features may lead to spurious detections of N_2^+ and wrong estimates of the strength of this band. The potential for blending, coupled with the weakness of the N_2^+ feature even when it exists, point to a need for caution in interpretation.

Thus, at this point, we have contradictory evidence for the ratio of N_2/CO . At least in the active outer regions of Hale-Bopp and deVico, these comets appear to be very depleted in N_2 relative to CO. The observations of Halley by Wyckoff and Theobald

(1989) also pointed to a depletion of N_2 for Halley. Indeed, Wyckoff *et al.* (1991a) derived a nitrogen depletion for comet Halley of a factor of ~ 6 relative to the Sun. Owen and Bar-Nun (1995) have pointed out the strong temperature dependence of trapping of N_2 and CO. Comets for which the deposition temperature was greater than 50K could trap progressively less CO and N_2 . However, H_2CO will continue to be trapped in comparable quantities to ices deposited at 50K. Thus, there would continue to be a source of CO, but the N_2 will be depleted relative to the CO.

Perhaps the solution to the quandary of depleted nitrogen is that our assumption that the solar nebula preferentially condenses nitrogen into N_2 instead of NH_3 is incorrect. However, observations of dense molecular clouds (Womack *et al.* 1992) have shown that $N_2 \gg NH_3$ for these potential star-forming sites. Another possibility is that the comets formed with much more molecular nitrogen but that it was depleted post-formation. It is certainly true that comets will deplete volatile gases in their outer layers as they pass close to the Sun, but this cannot be used as an explanation when comparing comets with similar orbital histories, such as Halley and deVico or Hale-Bopp and Bennett and C/1987P1 (Bradfield), which show discrepant ratios of N_2^+/CO^+ . Indeed, Engel *et al.* (1990) conclude that there might be some post-formational processing of Halley, but not to any large extent because of the low internal temperatures which are derived from the spin temperature of H_2O (Mumma *et al.* 1993). They point out, however, that gas can be trapped in water ice efficiently, but only if the ice is amorphous, such as it is in the various laboratory experiments. They conclude that codeposition into amorphous ice is unlikely to be a favorable mechanism in forming cometary ices since the water ice condenses, for most solar nebula models, at 140–160 K, at temperatures where the ice is likely to be crystalline and to not adsorb volatiles readily. However, the D/H ratios of H_2O and HCN suggest that cometary deposition temperatures were not as warm as Engel *et al.* posit.

In summary, in this paper we presented evidence of two comets for which no N_2^+ was detected, along with stringent upper limits, which would indicate that these comets are depleted in N_2 relative to CO. These observations are at odds with our understanding of the formation processes of ices in the solar nebula. Either a mechanism must be found to deplete the N_2 ice once formed or we must understand how a gaseous cloud with $N_2 \gg NH_3$ formed ices which do not contain much molecular nitrogen. Since we believe that N_2 will be deposited into H_2O ice in a manner which is similar to Ar, understanding this process has important implications for understanding the role of comets for delivery of noble gases to the terrestrial planets. It is therefore important that more unambiguous observations of the ion tails of comets be obtained, when possible, to determine the intrinsic values of N_2/CO in comets.

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Table I: Observational Parameters

Comet	Date	R_h (AU)	Δ (AU)	\dot{R}_h (km/sec)	$\dot{\Delta}$ (km/sec)	Distance		Start (UT)	Exposure (sec)
						Tailward (arcsec)	(km)		
deVico	3 Oct 1995	0.66	1.00	-3.4	-14.3	0	optocenter	11:37	600
						0	optocenter	11:57	600
	4 Oct 1995	0.66	0.99	-2.3	-12.9	0	optocenter	11:11	1500
						100	71,775	11:42	1200
Hale-Bopp	6 Apr 1997	0.92	1.40	2.9	18.4	0	optocenter	1:37	120
						10	10,150	1:46	900
						100	101,500	2:25	1800

Table II: Results

Comet	CO ⁺ (counts)	N ₂ ⁺ Upper Limit ^a	N ₂ ⁺ /CO ⁺ Upper Limit ^b
deVico	718	2.7	3.0×10^{-4}
Hale-Bopp ^c	1434	1.7	9.9×10^{-5}
Hale-Bopp ^d	1306	1.0	6.5×10^{-5}

Notes:^a 3910.9–3914.33Å bandpass^b Corrected for order sensitivity (see text)^c 10 arcsec tailward^d 100 arcsec tailward

Table III: Estimates from Earlier Spectra

Comet ^a		Intensity N ₂ ⁺ /CO ⁺ (4,0) ^b	Molecules N ₂ ⁺ /CO ⁺	1/a _o (AU ⁻¹) ^c	Type ^d
C/1908 R1	Morehouse (1908 III)	≥ 0.7	≥ 0.06	0.000174	pg
C/1940 R2	Cunningham (1941 I)	≥ 0.5	≥ 0.04	0.000001	pg
C/1947 S1	Bester (1948 I)	0.6–1.0	0.05–0.09	0.000024	pg
C/1956 R1	Arend-Roland (1957 III)	> 1	> 0.09	-0.000531	pg
C/1957 P1	Mrkos (1957 V)	0.2	0.02	0.002001	pg
C/1961 R1	Humason (1962 VIII)	0.2–0.3	0.02–0.03	0.004935	pg
C/1969 T1	Tago-Sato-Kosaka (1969 IX)	≤ 0.3	≤ 0.03	0.000507	pg
C/1969 Y1	Bennett (1970 II)	0.1–0.3	0.008–0.03	0.007082	pg
C/1973 E1	Kohoutek (1973 XII)	0.8	0.07	0.000020	FTS
C/1975 V1-A	West (1976 VI)	0.1	0.008	0.001569	IT
1P/1982 U1	Halley (1986 III)	< 0.1	< 0.008	0.055737	pg, CCD, ret
C/1986 P1	Wilson (1987 VII)	0.8	0.07	-0.000260	CCD

Notes:

^a Old designations listed in parentheses besides name^b Claude Arpigny – personal communication^c From Marsden and Williams (1995)

1/a (osculating) for Arend-Roland, Bennett, Halley and Wilson

^d pg=photographic;FTS=Fourier Transform spectrometer; IT=Image tube;

CCD=Charge Coupled Device; Ret=Reticon

Figure Captions

Figure 1: The spectral region of the CO^+ (2,0) and CH^+ (0,0) bands for Hale-Bopp. The positions of lines within this bandpass are marked, though not all marked lines are present. The pattern of detected vs. non-detected lines can be explained by the excitation levels of these molecules.

Figure 2: The spectral region of the CO^+ (2,0) and CH^+ (0,0) bands for deVico. The spectral orders are longer for the $R=60,000$ mode so more CH^+ lines were detected. Note that CH^+ is stronger relative to CO^+ in deVico than in Hale-Bopp.

Figure 3: The spectral region of the N_2^+ (0,0) band for Hale-Bopp. In addition, the C_3 (0,2,0)–(0,0,0) band is in this spectral region. The expected positions of lines for both of these bands are marked. There appears to be a feature at 3914.5\AA , which we tentatively attribute to C_3 , not N_2^+ .

Figure 4: The spectral region of the N_2^+ (0,0) band for deVico. As with Hale-Bopp, there appears to be a feature at 3914.5\AA . However, we believe this feature is just noise.

Figure 5: An optocenter spectrum of deVico, including the region of the (0,0) band of N_2^+ . Several C_3 bands and the CH B-X (0,0) band are identified. Additional, unidentified, C_3 bands are probably present. We show this spectrum to show the abundance of C_3 in this comet.

Figure 6: Simulated N_2^+ data. The upper panel shows an actual spectrum of Hale-Bopp. The positions of the potential N_2^+ lines are marked beneath it. The lower panel shows this same spectrum but with a “fake” band replacing the data between 3913 and 3914\AA . The fake band would have enough counts so that the ratio of N_2^+/CO^+ would equal the value detected for Halley. In the real data, there are some upward excursions which do not correspond to any N_2^+ lines. Even integrating just these upward excursions yields only $1/4$ the necessary counts.

Figure 7: Values for N_2^+/CO^+ as a function of $1/a_o$. The various ratios and limits are plotted in order to examine whether a trend exists with dynamical age of the comets. The prediction for this ratio of Owen and Bar-Nun (1985a) is shown as a dotted line. The open symbols are values derived from estimates of features in photographic and digital spectra, while the closed symbols represent measured digital spectra. See text for a discussion.

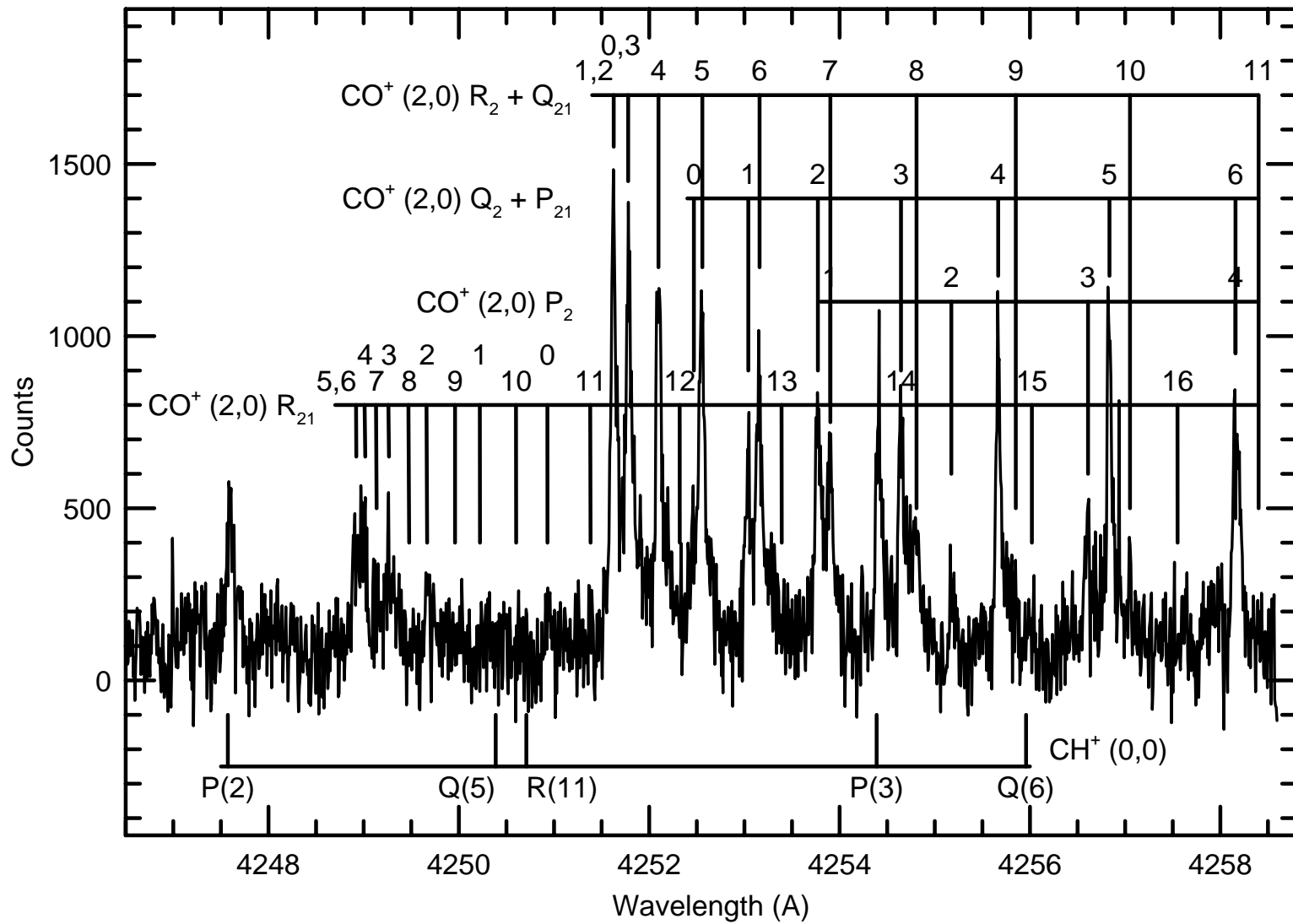


Figure 1: Cochran, Cochran and Barker

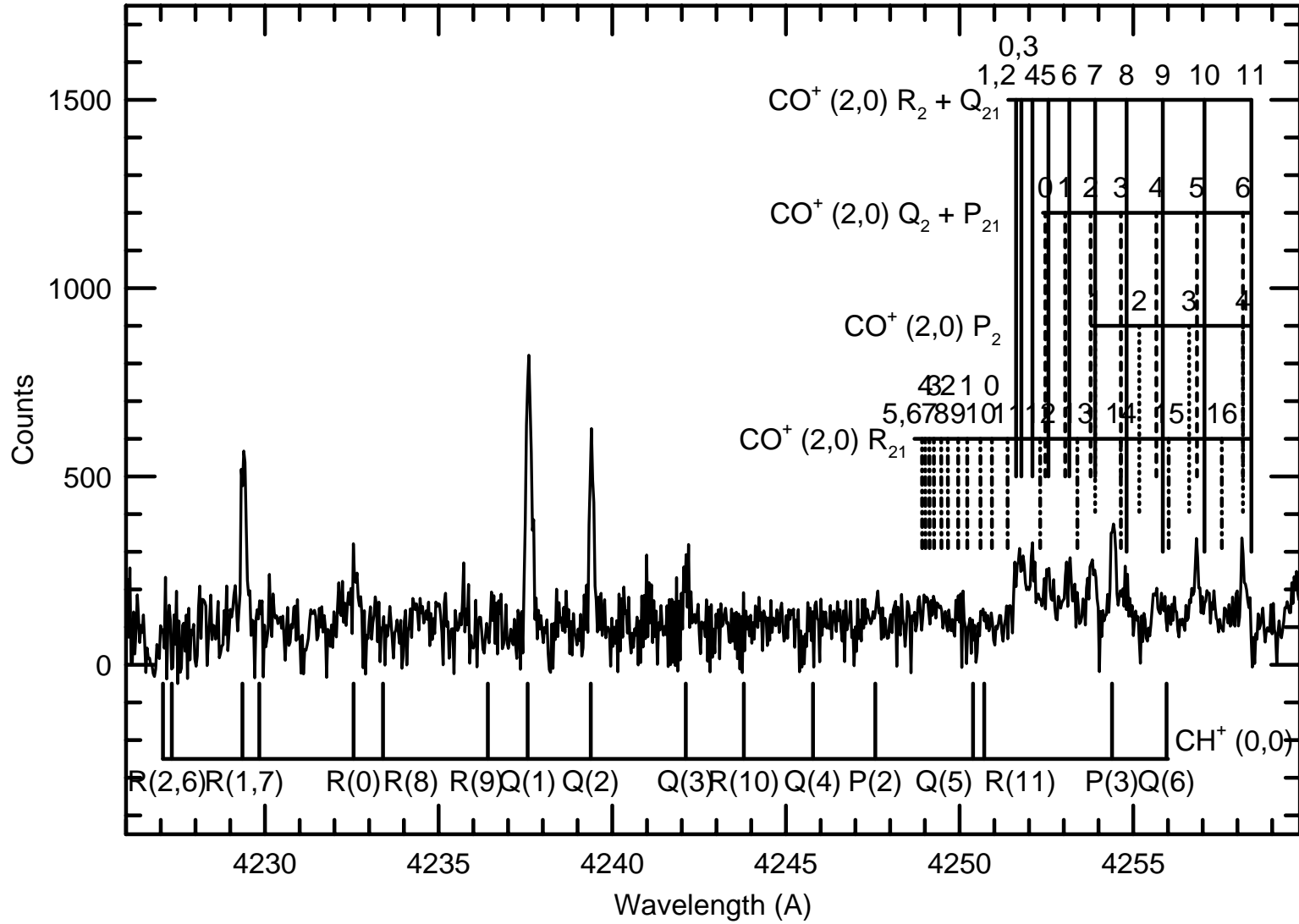


Figure 2: Cochran, Cochran and Barker

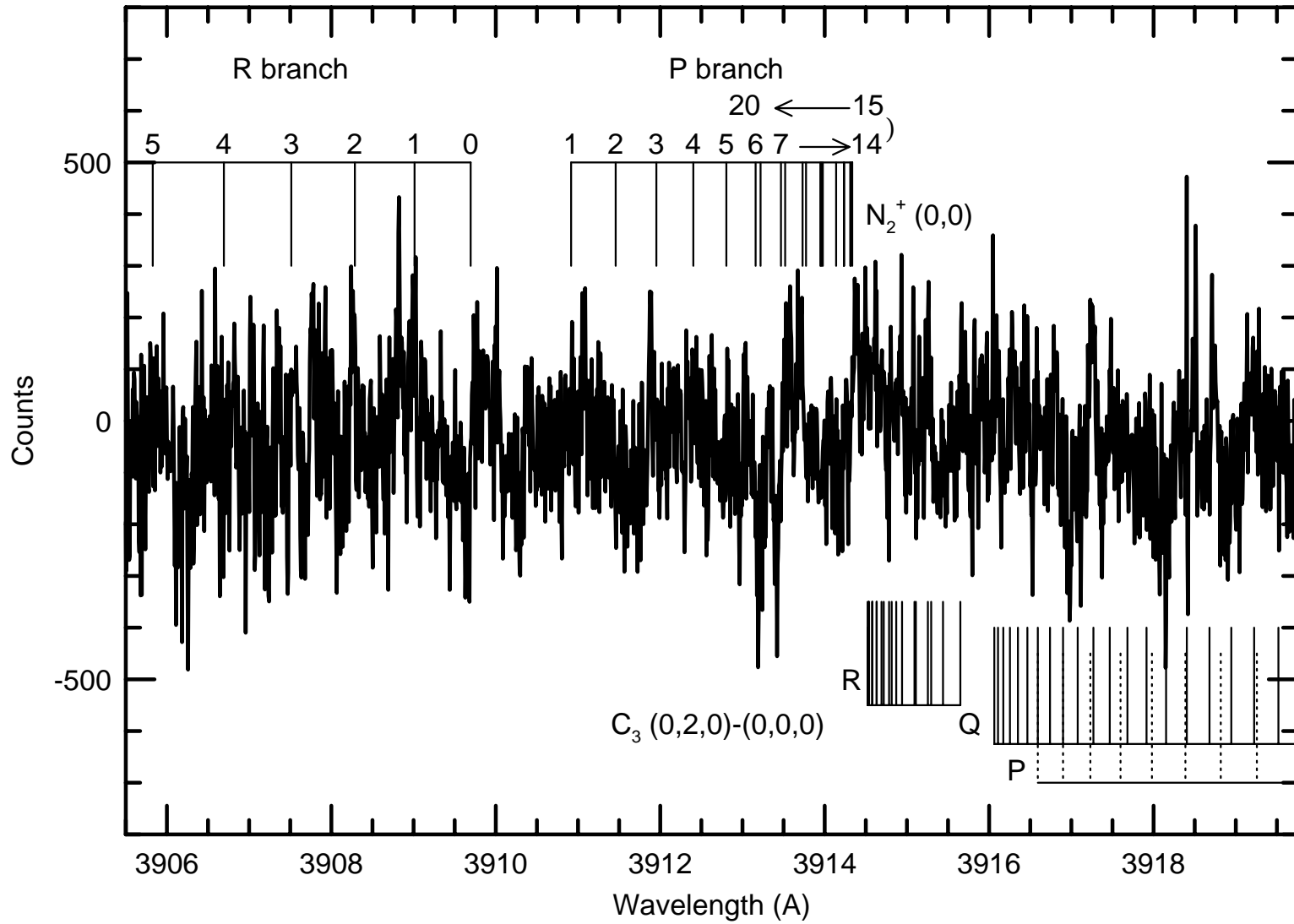


Figure 3: Cochran, Cochran and Barker

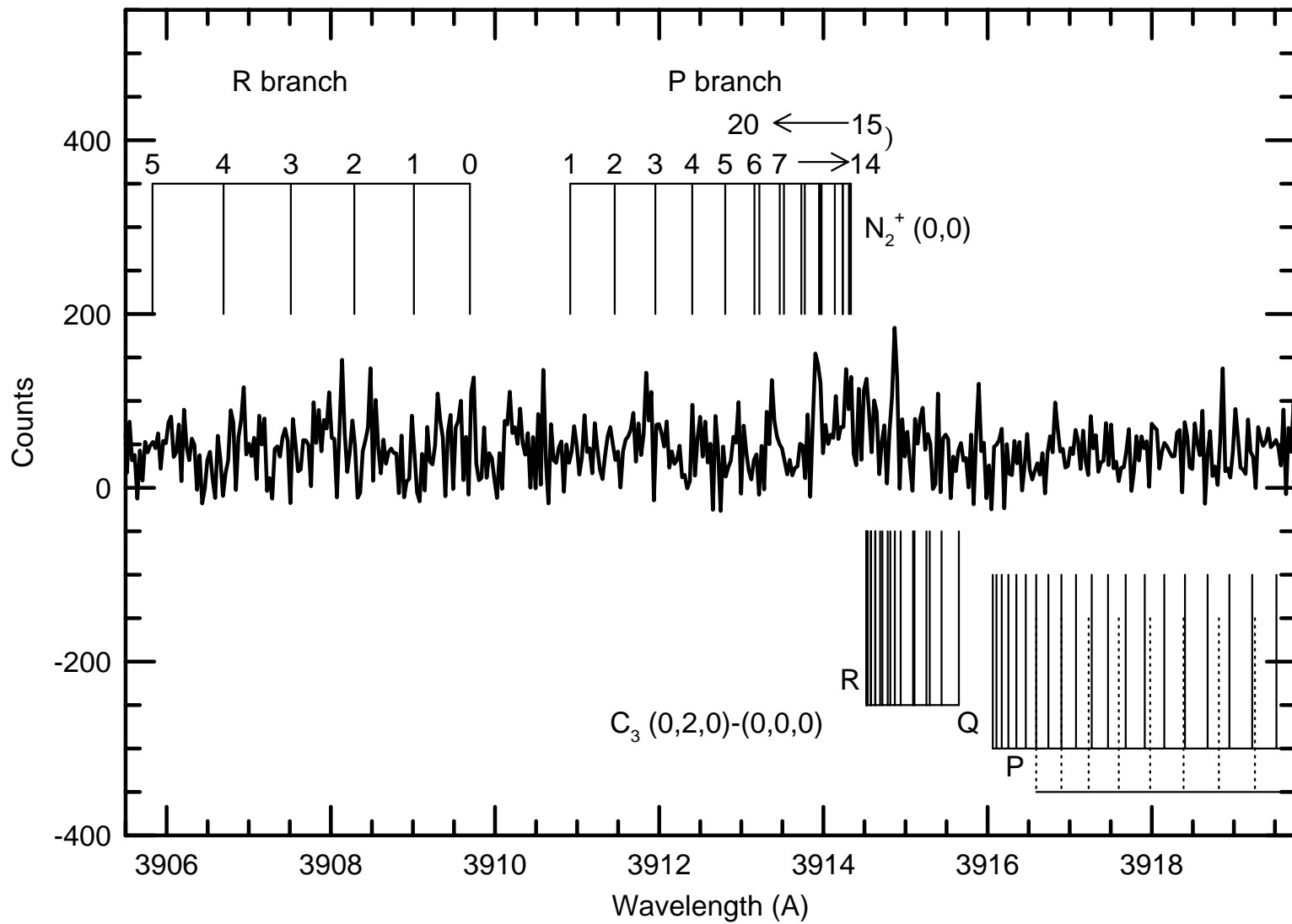


Figure 4: Cochran, Cochran and Barker

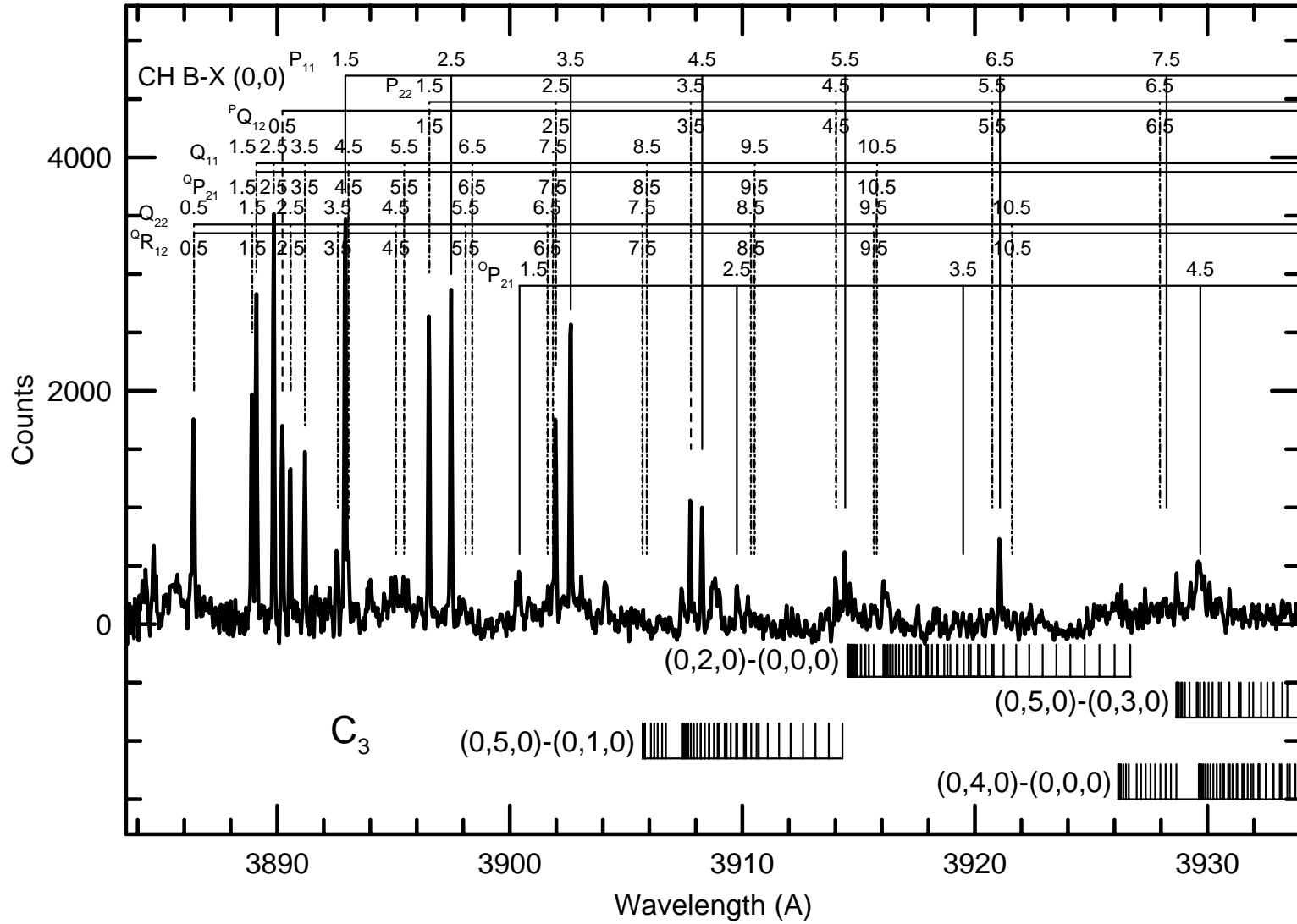


Figure 5: Cochran, Cochran and Barker

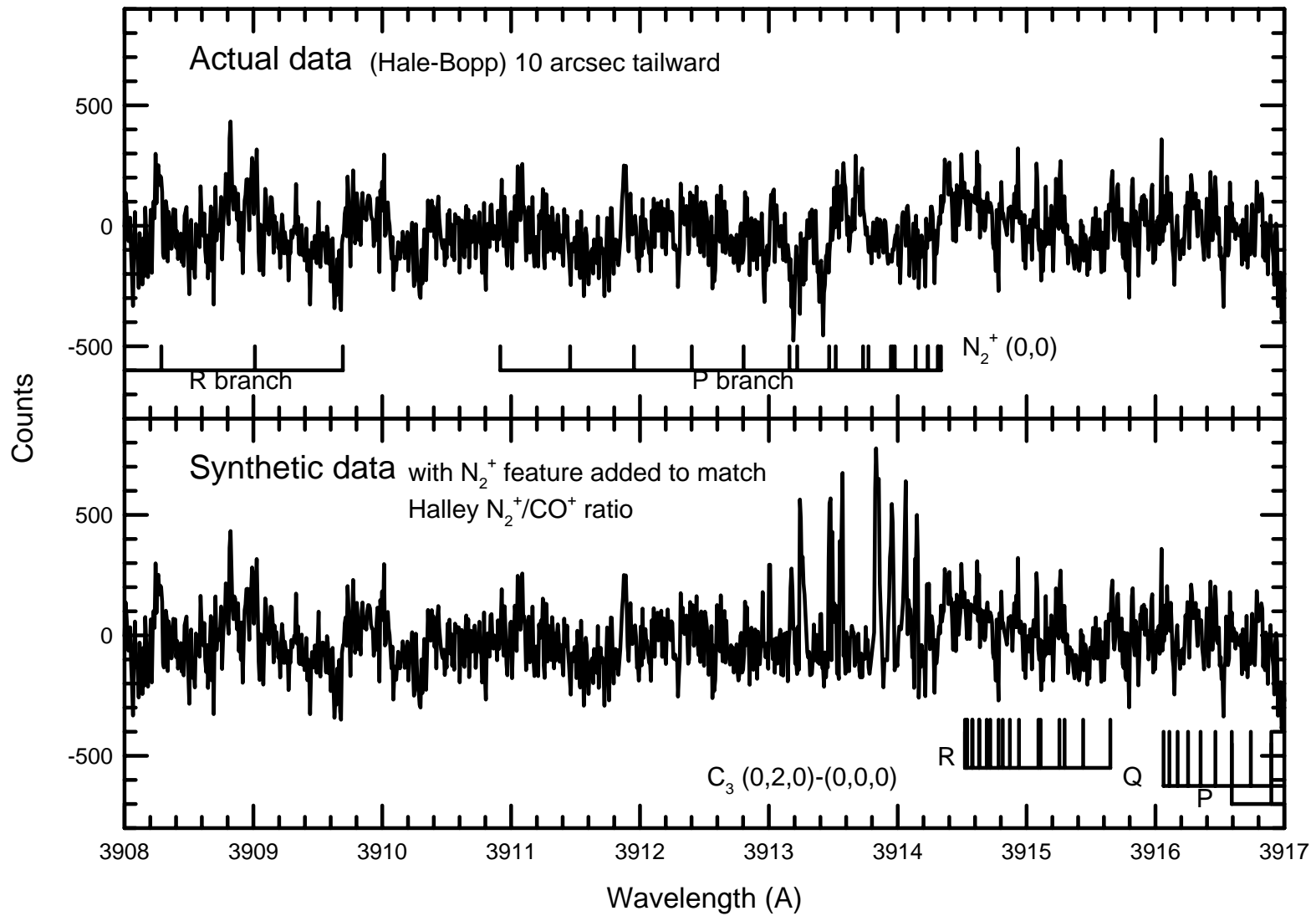


Figure 6: Cochran, Cochran and Barker

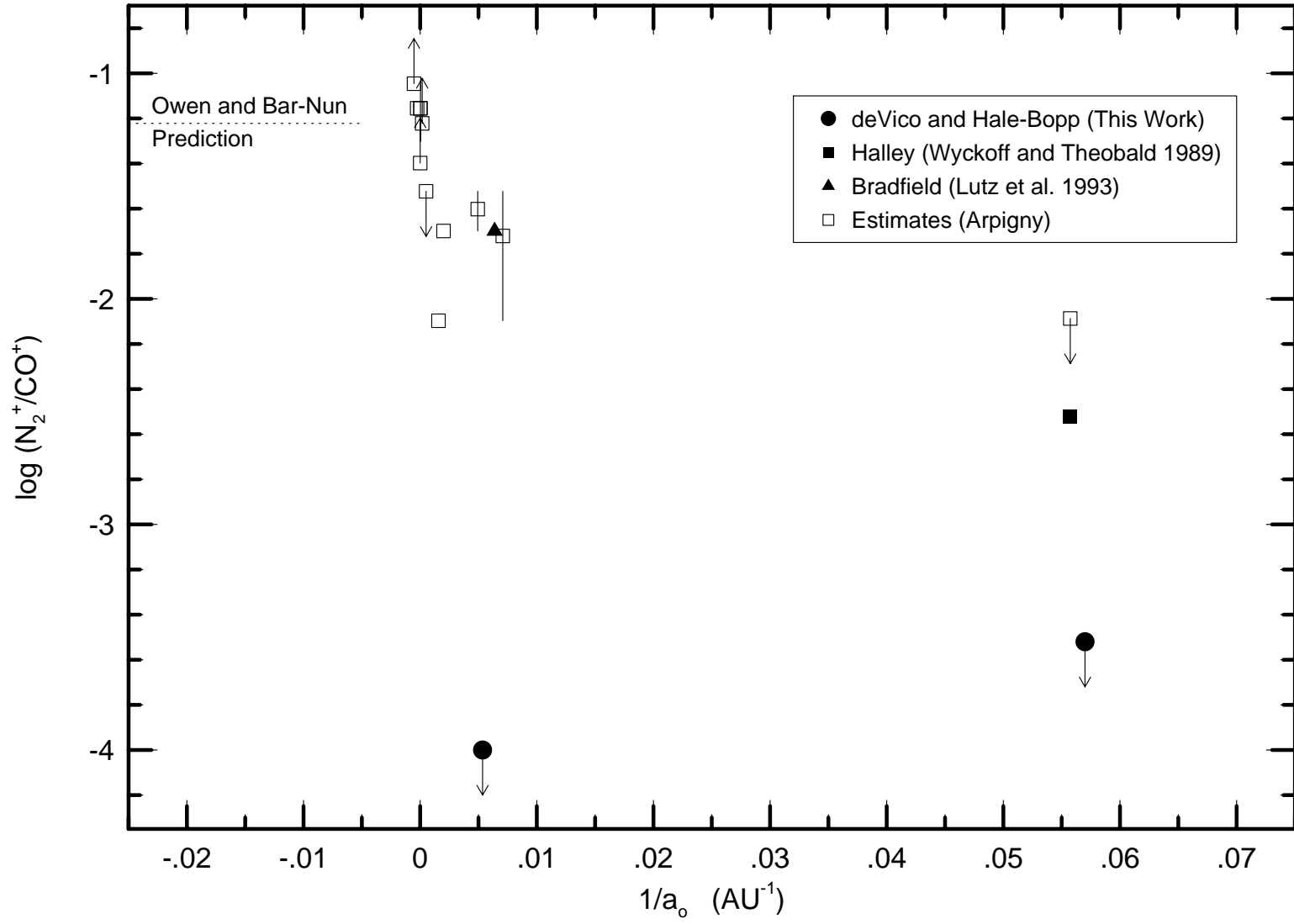


Figure 7: Cochran, Cochran and Barker