

REVIEW OF COMETARY SPECTRA

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Those investigators who have been active in cometary studies for a long time must by now have detected in their midst a number of interlopers from outside the solar system. As one of these newcomers from a far-off field of astronomy, who cannot possibly claim any expertise on comets, I feel compelled to account for the presence of stellar and interstellar astronomers in this arena. The reason is that some of us believe that the comets represent a sample of relatively unprocessed material from the early solar system, from which we may be able to learn something not only of the young sun and planets, but also something about the material of the parent interstellar cloud plus any fresher interstellar material that the cometary nuclei have been able to accrete over the past 4.6 billion years. The concept is hardly a new one; it probably began with Laplace, and has received increasing attention in the past decade as more information has accumulated from chemical and physical studies of condensed solar system material on the one hand, and from interstellar molecules and dust on the other. In the back of our minds, of course, there is also the thought: if the passage near the sun of a single small fragment of the condensible volatiles from the early solar nebula can result in a spectacular display such as we see in a bright comet, what is the chance that one can detect some trace of the same phenomenon in progress on a vastly greater scale around very young stars, still surrounded by very much larger quantities of similar material? Again this is not a new idea, but it is one reason for the intense interest that some stellar spectroscopists and early-stellar-evolutionists have developed in your subject

This should account for the fact that, in reviewing recent work in cometary spectroscopy and in recommending interesting tasks for the future, my point of view is less traditional and more speculative than is customary on occasions of this kind. Fortunately, Dr Arpigny and others will appear later in this program and provide you with solid information on what can be concluded with certainty from the analysis of cometary spectra.

The recent apparition of Comet Kohoutek 1973f drew a great deal of very desirable scientific attention to this area. Although weather conditions and position in the sky were both unfavorable when the comet was at its brightest, a most impressive amount of spectroscopic material was collected. I want to call special attention to the fine work on the spectrum by Benvenuti and Wurm and by Wehinger and Wyckoff presented to this Colloquium. These contributions demonstrate how much valuable work can be done with telescopes of only moderate size (1.22 m [48-inch] at Asiago, 1.0 m [40-inch] at Wise Observatory) when used with intelligence and energy

Both Comet Kohoutek and its contemporary, Comet Bradfield 1974b, were favorable for studies of the line spectrum of the coma because of the relatively low dust level as compared to recent very dusty comets such as Mrkos 1957d and Bennett 1969i. Nevertheless, although there are some 800 emission lines measurable on the Lick coude spectrograms of Kohoutek between 4800 and 8600 Å, I was surprised that there is in this material so little positive information on new constituents of the coma. Most of the additions to the comprehensive list of identifications in Comet Mrkos 1957d published by Greenstein and Arpigny (1962) are weak rotational lines of CN, C₂ and NH₂

It is worthwhile, I think, to mention briefly several molecules that were not detected in Comet Kohoutek on the Lick plates of 1974 Jan. 9, on account of their possible relevance to theoretical studies of the spectrum.

The Phillips bands of C_2 have as lower level the ground electronic state ($x^1 \Sigma_g^+$) of the molecule, which lies 0.08 eV below the lower state of the Swan bands. The Phillips system has apparently not been identified in comets.* On the 34 Å/mm Lick plates of Comet Kohoutek, there are a number of rather weak emission features between 7740 and 7860 Å which coincide with rotational structure of the 3-0 band as measured by Phillips (1948) and by Ballik and Ramsay (1963). However, some laboratory NH_2 bands also occur in the same region, and are expected to be of detectable strength in the Comet. Until an analysis of this NH_2 structure becomes available, the C_2 identification remains only a possibility. The 2-0 Phillips band with head at 8751 Å falls in a less confused region, but lies off these spectrograms. A search was also made for bands of the red system of CH_2 . A few coincidences were found between the list of laboratory features by Herzberg and Johns (1963) and weak unidentified cometary emissions, but there was no persuasive consistency. Certainly the red system of CH_2 , if present at all, occurs in only marginal strength. The HCO molecule also is of interest in connection with cometary chemistry; the most favorable band for its detection in the optical region is probably 070 - 000 of the red system near 6780 Å. This band has been measured in the laboratory by Herzberg and Ramsay (1955); their v_2' numbering has been changed by one unit by Johns, Priddle and Ramsay (1963). No trace of this structure was

* I am grateful to Dr Arpigny for calling to my attention the desirability of observations of the Phillips bands.

seen on the Lick spectrograms. The HNO molecule might also occur in comets; the strongest bands would probably be 000 - 000 and 010 - 000 which fall in the 6800 - 7500 Å region. Although a number of weak unidentified cometary emissions were measured in this range, none coincide with the structure of these HNO bands as observed in the laboratory by Dalby (1958).

The lines in Comet Kohoutek that were subsequently identified with H_2O^+ by Herzberg and Lew (1974a, 1974b) do not occur in Greenstein and Arpigny's line list for Comet Mrkos. The absolute intensity of the H_2O^+ features is greatest near the nucleus of Kohoutek, but there they are superposed upon the strong scattered solar continuum, so that they become relatively more conspicuous farther out in the coma, and especially in the tail. Wehinger and Wyckoff have measured H_2O^+ and CO^+ band intensities in the tails of both Kohoutek and Bradfield over a range of heliocentric distance (r). They find that the H_2O^+ column density in Kohoutek was five times that in Bradfield, under the same conditions. Similarly, Benvenuti notes that while H_2O^+ was strong in the tail of Kohoutek, Comet Bennett 1969i when observed with the same equipment at the same r showed no comparable H_2O^+ . There thus seems to be a spread in the H_2O^+ strengths of different comets. This appeared first in the results of Miller (1962, 1964), who was the first to call attention to these unidentified features in the red, and noted that they were especially strong in Comet Ikeya 1963a. Fig. 1 shows a low-dispersion Lick spectrogram of that Comet (this plate was in fact taken at the instigation of Dr. Miller), with the principal H_2O^+ features marked. Thus these cometary lines had been known to astronomers for years, awaiting only the laboratory work by Herzberg and Lew to solve the puzzle. I return later to speculation on why comets might differ in their H_2O contents.

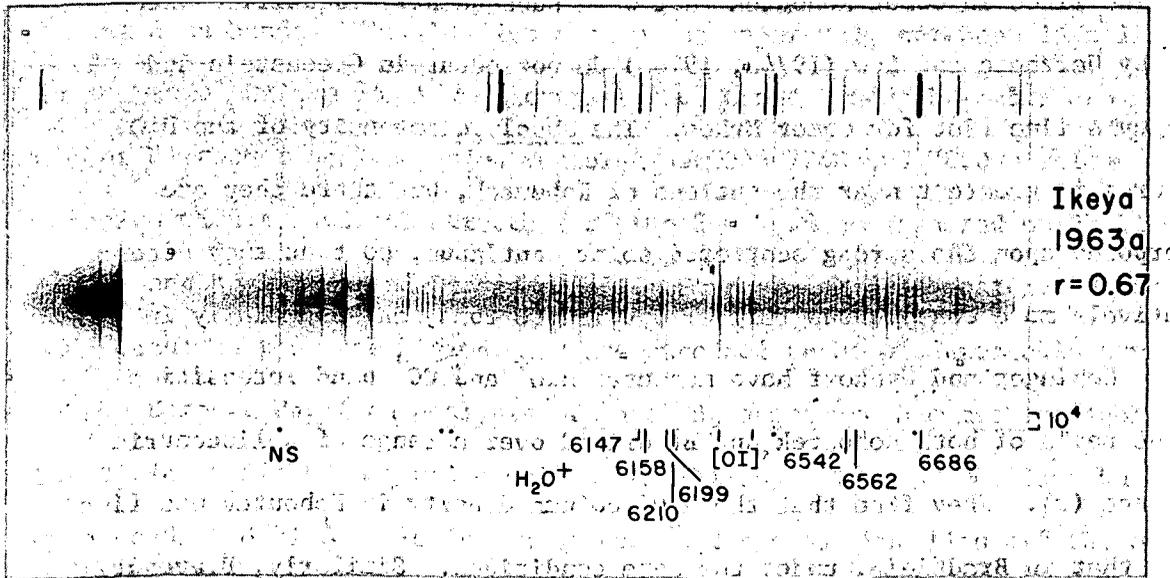


FIG. 1. The spectrum of Comet Ikeya 1963a in the region 5400-6800 Å. The spectrogram was taken by A. E. Whitford with the prime-focus spectrograph of the Lick 120-inch reflector on 1963 March 19. The original dispersion was 93 \AA mm^{-1} . This plate has been described by F. D. Miller (1964). A number of features now known to be due to H_2O^+ are marked with their wavelengths. The features marked by dots along the lower edge are due to either natural or artificial airglow; that on the left marked "NS" is $[\text{O I}] \lambda 5577$. The $[\text{O I}]$ lines at $\lambda\lambda 6300, 6363$ (here marked "[O I]") originate in the coma but weak airglow emission extending the full length of the 4' slit is also present. The brackets on the right lower corner indicate the distance on the spectrogram corresponding to 10^4 km at the Comet.

H_2O^+ is therefore to be added to the list of other molecular ions observed in comets, particularly in the tails: CO^+ , N_2^+ , OH^+ , CH^+ , CO_2^+ . I must mention in this connection the recent high-dispersion work by Fehrenbach and Arpigny (1973) on the structure of bands of OH^+ and CO^+ in Comet Bennett 1969i. The presence of CO_2^+ in comet tails (the strongest bands are at 3509 and 3674 Å) was established about 1948, but a detailed investigation of their structure in comets is still lacking. It seems to me that a reexamination of cometary spectra in the 3100 - 3800 Å region is overdue. For weak features we still lean heavily on the early McDonald work by Swings and his collaborators, 35 years ago. A repetition of this work at adequate dispersion will not be easy because the solar flux, which sets the intensity ceiling on fluorescent lines, is falling off rapidly in the near ultraviolet. Furthermore, the terrestrial airglow spectrum is very strong in this region, but here we do have the advantage that techniques for the subtraction of such a background are now commonplace. If close attention could be given to this region, one would not be surprised to find CN^+ (at 3185, 3063 Å) or N_2O^+ (at 3558 Å) or the near-ultraviolet bands of formaldehyde. The strongest bands of some interesting polyatomics which contain the CN radical also lie in this part of the spectrum: NCN and CNC (near 3300 Å) and HNCN (at 3440 Å). Conceivably, even the spectrum that has been attributed (Meinel 1972) to C_2^+ at 2490 Å might be detectable from outside the atmosphere.

At somewhat less difficult wavelengths, one should look carefully for NH^+ (probably the band at 4348 Å would be strongest) and H_2S^+ (an extensive electronic system like that of NH_2 and H_2O^+ lies in the blue-violet: see Duxburg, *et al.* 1972) and C_4H_2^+ (although its strongest band at 5068 Å will be confused with C_2)

The yellow, red, and near-infrared regions of the cometary spectrum are now being re-explored with respectable resolution, largely as a result of the availability of image intensifiers (with S25 and extended S20 cathodes) which offer large speed advantages over conventional photographic emulsions at the longer wavelengths. As a result, the presence of the red system of CN is now well established in Kohoutek and Bradfield. The 2-0 sequence has been well resolved, and Potter, et al. at this Colloquium report the detection of the 0-0 band near 1.1μ , and possibly 0-1 as well. The general decrease in oscillator strengths toward the infrared, as well as the fall-off in solar flux, militates against the presence of fluorescence transitions of high intensity in the infrared, unless compensated for by high abundance. Thus one hopes that a search will be made for the electronic bands of HO_2 in the 1.4 to 2.0μ region (Hunziker and Wendt 1974; Becker, et al. 1974) of the next bright comet. The low oscillator strength of vibration bands hinders their observation in comets, although the 5-2 band of OH at 1.08μ was detected by Meisel, et al. in Kohoutek. Certainly strenuous efforts should be made to observe the CO fundamental and first overtone (4.7 and 2.3μ) at the next opportunity.

Appreciation of the great amount of atomic H in comets (from $\text{L}\alpha$) led to attempts to detect $\text{H}\alpha$, and indeed a surprisingly strong emission line very near the proper wavelength (6562.82 \AA) was present in both Kohoutek and Bradfield. First seen (Donn 1973) in Kohoutek, it is also discussed here in a paper by Lanzerotti, et al. Unfortunately, a fairly strong pair of lines due to H_2O^+ occur at 6562.67 and 6562.80 \AA (Wehinger, et al. 1974). In Kohoutek, I had the impression that there must be some contributor other than H_2O^+ at that wavelength, because the 6562 \AA line shows a stronger

concentration to the nucleus than do the nearby H_2O^+ lines. But the amount of $\text{H}\alpha$ contribution can be assessed only when the H_2O^+ lines are subtracted out properly. If $\text{H}\alpha$ is present, presumably the $n = 3$ level is excited by solar $\text{L}\beta$ which, according to Feldman, et al. (1974 and this Colloquium) may also be responsible for the emission of $\text{O I } \lambda 1304$ which they observed in Kohoutek. This fluorescent cycle in O I initially populates the $3d^3D^{\circ}$ level, which then decays through emission of $\text{O I } \lambda 11287$, followed by $\lambda 8446$. No observations of $\lambda 11287$ have been reported, but the 8446 \AA region of Kohoutek is well exposed on a Lick spectrogram taken at a time when the 6562 \AA feature was strong. There is no hint of emission at 8446 \AA . Whether this fact can be reconciled with the intensities of $\text{H}\alpha$ and $\text{O I } \lambda 1304$ awaits detailed calculation.

Today there can be no doubt from modern large-scale, high-dispersion spectrograms that $[\text{O I}] \lambda\lambda 6300, 6363$ are present in cometary comae; they were very strong in Kohoutek. It will be recalled that confusion with airglow lines was a serious problem on older spectrograms. The physical mechanism responsible for the population of the upper levels of these lines leans on the question whether the green line of $[\text{O I}]$ at 5577.35 \AA also is present or not. Airglow contamination is here more serious, as is the fact that the line falls in the complex structure of the very strong 0-1 sequence of C_2 Swan bands. Its separation from these sources of confusion is a difficult matter, even at high dispersion. In Comet Kohoutek, a sharp line is indeed present at 5577 \AA in the center of the coma. There is no confusion with airglow on this spectrogram. The $[\text{O I}]$ wavelength falls in a gap in the 0-1 C_2 rotational structure, precisely between two strong blended emissions near 5576.0 and 5578.7 \AA . However, a blend of

three weak rotational lines of the 1-2 band essentially coincides with [O I], and until some observational or theoretical means is found to subtract their contribution, I see no way to make an estimate of the strength of the green [O I] line. Perhaps the best determination of the population of the 1S level of O I will be by observation from above the atmosphere of the [O I] line at 2972 Å.

The region of the [N I] pair at 5197.94, 5200.41 Å is well exposed on one Lick 16 Å/mm spectrogram of Comet 1973f. Unfortunately two weak NH₂ lines occur at 5199.41, 5199.78 Å, and are seen on this plate as a faint fuzzy emission which effectively masks the [N I] positions. Nevertheless, one can be certain that if the [N I] lines are present in this Comet, they must be two orders of magnitude weaker than [O I] λ6300.

The possibility of observing the absorption spectrum of a comet has often been discussed. A campaign to observe the occultation of bright stars by Comet Kohoutek was organized through the cooperation of Dr. B. G. Marsden, but the effort was unsuccessful. This was perhaps not surprising when one considers the number of constraints: the star must be bright enough, of sufficiently early spectral type, the event must occur on a clear night at a time when the star is adequately far above the horizon at an observatory where the interested spectroscopist has access to the telescope... It might be useful to point out here what the aim and the expectation of such an experiment would be. It is quite certain that for ordinary molecules, the absorption lines will be exceedingly weak. Thus, Arpigny (1965) found that at a projected distance of 10^4 km from the nucleus, the largest value of the CH column density in the comets he studied was $5 \times 10^{11} \text{ cm}^{-2}$. If all these CH molecules were in the ground rotational

state, even then one would expect an equivalent width for the 4300.32 Å absorption line of CH of only 0.3 mÅ, which is undetectable by conventional methods. The best case is CN; Arpigny's largest column density is $2.5 \times 10^{12} \text{ cm}^{-2}$, from which one predicts the line 3874.61 Å to have an equivalent width of about 7 mÅ. Thus one does not expect conspicuous molecular absorption lines in comets, particularly since the interference by the overlapping emission line will be serious; possibly it could be taken out by a 2-channel technique. Despite the difficulty, I think the observation would be worthwhile as a useful check. A more interesting possibility is, however, that one might in this way be able to detect in absorption some polyatomic species which do not occur in emission at all, on account of predissociation in the upper state. In addition, I have pointed out elsewhere (Herbig 1975) the curious fact that although essentially all the atoms and molecules which are found in interstellar absorption are also found in fluorescent emission in comets (the sole exception being Ti II), the diffuse interstellar bands have never been observed in comets. It would be very interesting to determine whether they can be detected in absorption against a star seen through a cometary coma.

I also would like to suggest that serious consideration be given to the direct measurement of doppler shifts due to expansion or streaming motions in comets. Atomic hydrogen expansion velocities of about 8 km s^{-1} have been inferred from the theory of L α envelopes, but the expectation is for velocities of about 1 km s^{-1} near the nucleus for most species. Such shifts are probably in the realm of direct detection, given high spatial and spectroscopic resolution. Far out in the plasma tail, velocities in excess of 100 km s^{-1} are expected, and seem to be confirmed by the speed

of motion of tail structures. Lick spectrograms of Comet Bradfield showed no detectable doppler shifts in the tail a few minutes of arc from the nucleus, but I am told that that was to be expected. The observation deserves to be repeated as far out in the tail as possible.

Let me mention two other matters that should be called to the attention of cometary spectroscopists. First, the matter of how to determine whether a newly-found comet deserves special spectroscopic attention. If another of those extraordinary, CO^+ -rich objects like Comet Morehouse 1908 III or Humason 1961e should appear, certainly we should know about it as soon as possible. Such a spectrum is quite unmistakable even at low dispersion (see Fig. 2), and the diagnosis can be performed with even a moderate-sized telescope. I would like to recommend that encouragement and support be given to anyone who is prepared to embark upon a systematic program of this type.

Second, I am very curious as to the spectra of the so-called 'giant' comets, namely those having $q = 3$ to 5 a.u. Apparently the only such objects for which spectroscopic information is available are Comet Minkowski 1951 I ($q = 2.57$) and Comet Baade 1955 VI ($q = 3.9$). Comet 1951 I had a weak CN $\lambda 3883$ on an intense solar continuum, while 1955 VI showed only a slightly-reddened continuum (Walker 1958). Surely such comets need more attention, particularly in the red. There will be an opportunity for more such observations in 1975 during the apparition of Comet Lovas 1974c, of $q = 3.01$. Unfortunately for northern observers, it will be located in the far southern sky before perihelion passage (on 1975 Aug. 22), but spectroscopic attention from either hemisphere is recommended.

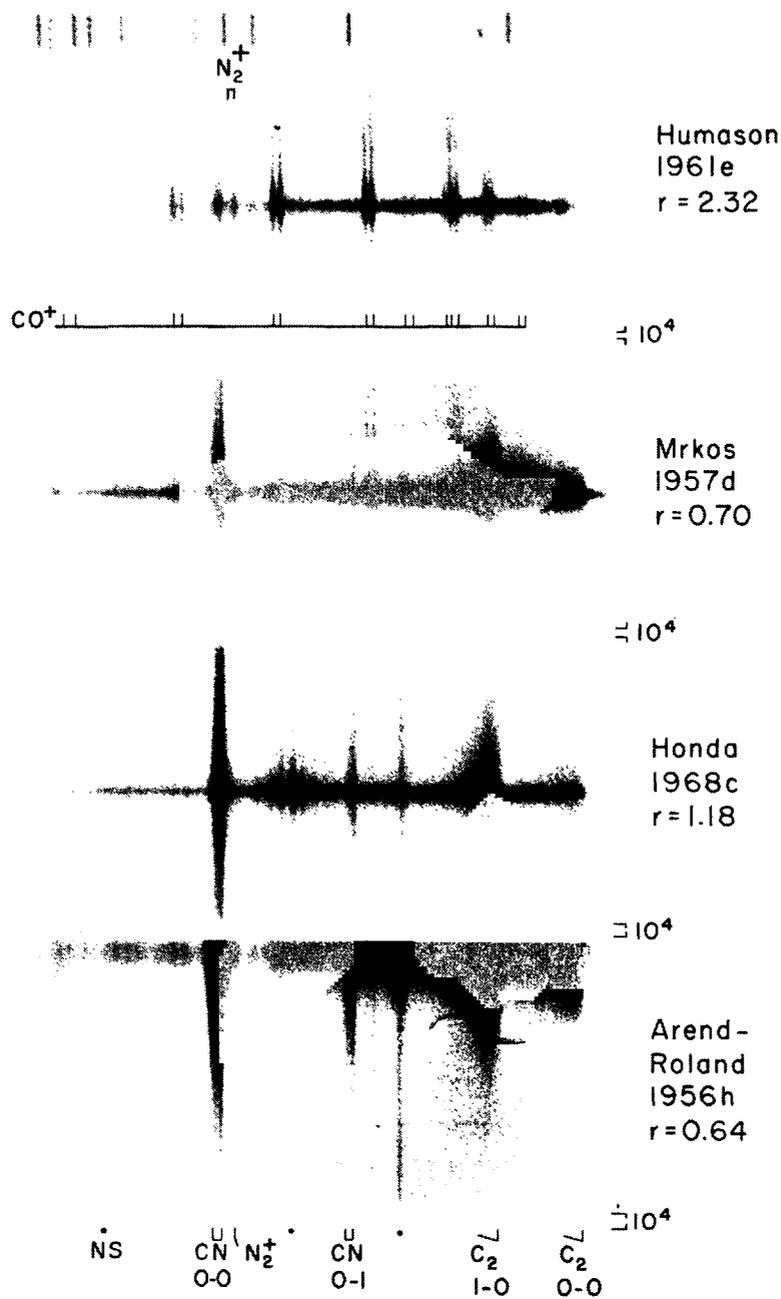


FIG. 2. A series of cometary spectra chosen to illustrate the wide range in intensity of the CO^+ emissions (marked below the spectrum of Comet Humason, upper panel) in different comets. The features marked with dots at the lower edge of the figure are Hg lines from artificial lighting. The original negatives were taken with the Crossley reflector, at a (prismatic) dispersion of 350 \AA mm^{-1} at 3950 \AA . The brackets on the right side of each panel show 10^4 km at the distance of the comet.

Finally I would like to speculate upon the explanation for possible intrinsic abundance differences between comets. Here, I set aside chemical processing subsequent to the formation of the nucleus, and the effects of selective evaporation during perihelion passages, and focus on chemical effects in the original parent cloud

Fig. 3 shows how large such anomalies can be in the case of the C_2 , C_3 /CN ratio; these have been commented on by Swings and Haser (1956). But the CO^+ phenomenon is even more spectacular. Comets like Morehouse and Humason, already mentioned, showed very strong CO^+ emission even in the coma. But there is a large variation of CO^+ strength from one to another even among ordinary comets, which transcends the decrease in the CO^+/CN ratio as r increases. Fig. 2 shows this effect in a sample of recent comets, as observed at Lick with low dispersion. If we are here witness to a major dispersion in CO content from one comet to another, then there exists a well-known process which could account for it. The equilibrium between CO and CH_4 has often been discussed in connection with the chemistry of the original solar nebula, originally by Urey (see Anders 1972). If thermodynamic equilibrium can be maintained continuously in a cooling gas of solar composition (i.e., hydrogen in great excess), then the progressive diversion of carbon into methane is controlled by the reaction



which at a total pressure of 10^{-6} atmosphere causes $CO > CH_4$ if the temperature is above 550°K (Anders 1972). This is the ideal situation, however; laboratory experiments under simulated solar nebula conditions, with the gases in contact with realistic catalysts (the process goes very

Giacobini-
Zinner
1959b
 $r = 1.03$

$\times 10^4$

Burnham
1959k
 $r = 1.11$

$\times 10^4$

$\begin{array}{c} \text{CN} \\ \text{O-0} \end{array} \quad \begin{array}{c} \text{C}_3 \\ \text{CN} \\ \text{CH} \\ \text{O-1} \end{array} \quad \begin{array}{c} \text{C}_2 \\ \text{O-1} \end{array}$

FIG. 3. An illustration of the difference in C_2 , C_3 and continuum strengths between two comets having about the same CN intensity and heliocentric distance. The original spectrograms were taken with the same equipment used in Fig. 2.

slowly in the absence of a catalyst), the reaction does not run completely to methane, with its H/C ratio of 4. Rather a mixture of intermediate products with smaller H/C ratios are produced, ranging from C₂H₆ through C₂₀H₄₂. It is possible that the nuclei of CO-rich comets represent material that was withdrawn from the parent gas at a time when that gas was hotter than about 550°K. More conventional comets, on the other hand, may have condensed from gas in which the molecular equilibria were frozen-in at a lower temperature, and thus are dominated by a mixture of methane plus complex hydrocarbons. This material should be a ready source of volatile hydrocarbons when reheated, as well as of the H₂O which will also be abundant, according to eq. (1).

It would be useful to have an estimate of the relative abundance of N₂ and NH₃ in comets, as a check on these considerations. That is, a similar relationship



controls the concentrations of nitrogen and ammonia, but here the balance point is struck at a lower temperature: at 10⁻⁶ atm, N₂ > NH₃ for T > 280°K. Therefore one expects N₂ to be in excess in both CO-rich and CO-poor comets. It is interesting that laboratory experiments (Hayatsu, et al. 1972) which begin with a mixture of NH₃, H₂ and CO yield not only N₂, NO, and (CN)₂ but also HCN and CH₃CN, both of which were found in Comet Kohoutek.

On these grounds, one would expect that a CO-rich comet would be correspondingly H₂O-poor. When another comet like Humason or Morehouse presents itself, it will be worthwhile to determine the H₂O⁺ and OH strengths,

and if possible that of $L\alpha$ as well. In real life, of course one also expects to find many intermediate cases between these two extremes. In fact, if chondritic meteorites are a proper guide, one would expect that a cometary nucleus may have been assembled from materials having a variety of histories and CO/hydrocarbon contents, so that a pure sample of either extreme would be uncommon.

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DISCUSSION

F. L. Whipple: I would like to ask, in the case of comets as an aggregation of interstellar matter, what sort of reactions do you get there?

G. H. Herbig: You mean in the interstellar medium at this moment?

F. L. Whipple: Yes, like we see in clouds that are starting to form.

G. H. Herbig: The temperatures that we are concerned with here are above room temperature, 300 to 1000 Kelvin.

F. L. Whipple: I am talking about 10 degrees, 60 degrees, around there.

G. H. Herbig: I think that ordinary chemistry would go rather slowly at that.

But someone here is more informed on that subject than I. I am speaking about things that would occur in a primitive solar nebula in the presence of catalysts, and that is excruciatingly important.

So I really can't answer your question Fred, But I think there are people here who can.

B. Donn: The regions of the interstellar medium where you observe this complex array of molecules, are at temperatures not of 10 degrees or 20 degrees, but in fact a few hundred degrees centigrade, at concentrated regions with IR sources, compact H₂ regions and such.

So we are talking about temperatures almost comparable to Herbig's.

However, an important point about all these chemical reactions is that at pressures like 10⁻⁶ atmospheres - where for instance you have the interstellar medium density of up to 10¹³ - you will generally not get a thermodynamic equilibrium composition, because at these low pressures, you will not have a Boltzmann distribution of internal energy states of the molecule. They will radiate too fast for collisions to populate them.

Reactions generally take place from excited levels, not from the ground state. The rates of reaction and the processes are very dependent on having these higher states populated.

So one needs to know, in the case of a reaction you have written there, how these depend upon the excited vibrational states of the molecule, because the tendency in the experimental and theoretical results being developed now show that these results are very dependent on having excited vibrational states.

DISCUSSION (Continued)

Therefore, if you don't have them, the whole process is different than what we talk about in the laboratory. We have to be very careful about using laboratory results under these conditions.

It is just a new ball game.

G. H. Herbig: Well certainly a chemist should make those comments.

But all I wanted to say is, somehow, in the early solar system, this kind of chemistry was done on a very large scale, and we can't argue with that. You pick up a carbonaceous chondrite, and that is it.

Now whether that is relevant to the comets is a matter of opinion, of course.

E. Ney: On one of your slides, George, it looked to me as if Comet Bradfield had the continuum very much less pronounced at 0.66 AU than in the spectra just before it. And something drastic did happen to Bradfield in the short period there.

Did you happen to think that it was significant that the continuum was very much down in that bottom slide?

G. H. Herbig: One would have to know the exposure times, of course.

No, I haven't looked at the materials from that point.

E. Ney: Will you look at them, maybe?

C. B. Opal: With regard to detection of the 8446Å line of atomic oxygen: the oxygen coma is about 10^6 km across at 1 AU, as opposed to 10^5 km for molecular constituents, so it is difficult to see the oxygen line with a high f-number, high dispersion spectrograph. The line should be detectable with a suitable instrument.

M. Dubin: Dr. Herbig, in the general pattern of the chemistry and spectroscopy on the comets and the classifications you just described, would you comment on whether the distribution of comet spectra pattern themselves into the Oort thesis, you know, of inner solar system comet formation, and then storage in the outer solar system, or more in the Cameron picture?

Would you comment in any respect, on that?

G. H. Herbig: I am not competent to discuss that subject.

DISCUSSION (Continued)

W. Jackson: In terms of the oxygen green and red line, if water is present in comets, you have to get Oxygen ¹D from the photodissociation of water, because one of the primary processes in the region below 1500 angstroms, around Lyman alpha gives H₂ plus Oxygen ¹D.

And that is one of the likely sources of Oxygen ¹D in the comet coma.

J. T. Wasson: Your explanation of the variation in CO abundance in terms of the reaction



is missing one important effect—the relative volatilities of the different species. In the inner solar system (c. 5 AU) temperatures probably never fell low enough to allow CO or CH₄ to condense as pure substances. They could have condensed as clathrates, but in this case they would have been competing with each other and other substances for the guest position in the clathrate structure. Far from the sun ($\gtrsim 30$ AU) CO may have been able to condense in a relatively pure form. Thus the difference in CO⁺ abundance could be a measure of distance from the sun at which the comet formed.

A minor second point is that solar system abundance calculations indicate that O is about 1.5 times more abundant than C. Thus even if equilibrium conditions strongly favor the species on the left side of your reaction, about one-third of the nebular O will still be present as H₂O.

I think if the experience with meteorites means anything, (those, as you know are a complex mixture of granules, small domains having quite different histories) obviously the early solar system was a terribly complicated thing with involved time sequence of events.

I am saying that on the microscopic scale a process like CO - H₂O reaction might run, but a real comet or any real solar system body is a conglomerate of material having rather different histories. On the microscopic scale there may be enrichments or deficiencies due to local chemical effects, but the thing one actually observes in a real comet is the composite of the subsequent collection of a lot of these domains through processes of which we don't know very much.

So a comet like Humason may respond to considerations of this sort but perhaps only in a statistical sense. I don't mean that every gram of material in that object ran through this process to completion.

DISCUSSION (Continued)

You recall carbonaceous chondrites are a mixture of things having obviously quite different histories. Maybe the same considerations apply in the cometary world.

F. Dossin: About the red line of oxygen, I think that the Doppler shift due to the motion of the comet relative to earth should be sufficient even at conventional Coudé dispersion to distinguish between atmospheric and cometary lines.

G. H. Herbig: Yes. The red lines, at the time these first series of plates were taken, had a cometary red shift of about 40 kilometers per second, that unmistakably identified them as cometary.

L. Biermann: I would like to re-emphasize that if the cometary matter formed at large distances from the sun of several tens AU or more (cf. my contribution to the Barcelona Conference 1973, Problems in Origin of Life, August/September 1974)—then the conditions were greatly different from those chosen by Anders and co-workers in these model experiments aimed at simulating the origins of meteorites. It is of course conceivable that more than one kind of cometary nucleus exists depending on the place of their formation and that the carbonaceous chondrites have a composition and place of origin between other meteorites and cometary matter.

A. H. Delsemme: In respect to the possibility of a thermal equilibrium quenched and condensed from the solar primeval nebula, mentioned by Herbig, I wish to mention the remarks I proposed on this matter at the comet Kohoutek workshop a few months ago. In particular, many clues point to a rather low redox ratio. As a matter of fact, H/O should rather be in the vicinity of 3 in the volatile fraction of the cometary stuff, than in the vicinity of the solar abundance, which is three orders of magnitude higher. This is already implied by the simultaneous presence of H_2O^+ , with CO^+ , CO_2^+ and N_2^+ . The existence of HCN rather than NH_3 , and of CO rather than CH_4 , points either to the possible quenching of a rather high-temperature equilibrium, (1000 K) or rather to the absence of H which shifts the equilibria towards dehydrogenated products. Good assessments of the abundances of the major constituents of the cometary snows will bring a better answer to this interesting question.