1953AnAp...16...82R

CARBON STARS, COMETS AND COMBUSTION PHENOMENA

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Sommaire. — *La question de l'identification de la molécule responsable pour l'émission du* « *groupe* 4 050 » *dans les comètes et les sources terrestres et pour l'absorption de ce groupe dans les atmosphères des étoiles carbonées du type N avancé est examinée en détail. Les relations entre l'émission et l'absorption de ce groupe et les phénomènes observés dans les décharges, flammes et explosions ainsi qu'en pyrolyse et photolyse sont discutées. L'attention est attirée en particulier sur le fait que l'émission et l'absorption du* « *groupe* 4 050 » *sont toujours liées à la formation de particules de carbone* (*suie*). *Des arguments sont présentés en faveur de l'attribution de ce groupe* (*pour lequel un nouveau schéma vibrationnel est proposé*) *à la molécule* C_3.

Le rôle possible des particules de carbone dans les atmosphères des étoiles du type N avancé a été discuté. La possibilité a été envisagée d'interpréter la formation des molécules responsables pour l'émission du « *groupe* 4 050 » *dans les comètes par collision de protons d'origine solaire avec les surfaces des glaces organiques des noyaux ou avec des molécules carbonées sublimées qui se trouvent à proximité de ces surfaces.*

It has been known for a long time that the spectra of carbon stars and of comets present great similarities in the photographic region. In either case the main characteristics are the bands of carbon compounds CN, CH and C_2, which appear in absorption in the carbon stars, in emission in the comets. The similarity has been enhanced recently, when it was pointed out by McKellar [1] that certain absorption features of the late N-stars around λ 4 050 appear to be due to the same molecule as the emissions observed in comet spectra and usually designated as " 4 050 group ". Despite a great deal of experimental work performed during the last ten years the molecule responsible for the 4 050 group — which we shall call for brevity the 4 050 molecule — is not yet known with certainty. Moreover many aspects of the behavior of the 4 050 cometary emission remain mysterious. Recent laboratory investigations on flames, pyrolysis and photolysis have a direct bearing on the assignment of the 4 050 group and on its behavior. It is the object of this paper to present the status of the astronomical question and its relations to the recent experimental investigations.

The 4 050 group in comets

Almost all comets show a group of emission lines around λ 4 050 ; in certain objets these emissions stand out conspicuously. Their intensity relative to the emissions of CN, CH, C_2, OH and NH increases with heliocentric distance. At

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$r = 2.2$ A. U. the 4 050 group may still be strong while the CH - and C_2 - bands have completely disappeared [2]. Unlike the emissions of CH, C_2, and CN, the absolute intensity of 4 050 increases only slowly when the comet approaches the sun.

On low dispersion spectrograms the 4 050 lines appear sharp, like atomic lines or individual rotational components of a band. However a higher resolution [3] shows that the 4 050 emissions are definitely wider than individual rotational lines, such as those of CH, CN or OH : each 4 050 emission is really a " band " in itself.

The 4 050 emissions are observed only in the central part of the coma. However they are not quite so concentrated near the nucleus as the CH-bands [4], and their distribution within the head may differ appreciably from that of CH [2].

No line of the 4 050 group is found in interstellar absorption. This negative result excludes the assignment of 4 050 to an ionized diatomic hydride, like NH^+, such as had been considered at one time. If NH^+ had an electronic transition of high f-value in the region of 4 050 it would have been found in interstellar absorption.

Many fruitless attempts have been made to assign the 4 050 cometary group to a diatomic molecule (new system of C_2 ; tailbands of CN ; bands of CH, NaH, NH^+, etc...). Around 1942 the idea was raised [5] that the emission was probably due to a polyatomic molecule consisting of cosmically abundant atoms (H, C, N and O).

THE 4 050 REGION IN LATE N-STARS

The latest carbon stars present a very strong absorption shortward of approximately λ 4 400. This intensity drop has been observed long ago ; the early investigators (SHANE, 1920) noticed readily that the intensity decrease toward the ultraviolet was much greater than expected from the temperature indicated for late N-stars. The most recent investigations are those by SHAJN and STRUVE [6] ; by McKELLAR [7] and by SWINGS, McKELLAR and RAO [8]. The observations by SHAJN and STRUVE at the McDonald Observatory showed that the violet absorption was not really continuous, but, partly at least, of the molecular type. McKELLAR's low resolution spectrograms obtained at Victoria indicated striking wavelength coincidences between the main violet absorption maxima of the N-stars shortward of λ 4 100 and the strongest cometary emissions of the 4 050 group. The McDonald spectrograms of Y Canum Venaticorum, RY Draconis, U Hydrae and X Cancri obtained by SWINGS and RAO in April and May 1949 and discussed jointly with McKELLAR had a higher resolution than the Victoria plates and extended to much shorter wave lengths. Indeed a spec-

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trogram of YCVn extended to λ 3 300 and revealed strong new ultraviolet absorption bands centered near λλ 3 790, 3 700, 3 595, 3 480 and 3418. These bands are characteristic of late N-stars and are found neither in R - nor in late M - objects. This new material added substantial evidence in favor of the identity of the molecule responsible for the cometary 4 050 group and for the 4 050 absorption features in late N-stars. While this identity may not yet be considered as completely proved it appears established well enough to be used as a working hypothesis. This matter has been discussed summarily recently [8] ; details will be given in a forthcoming paper.

However the tremendous intensity decrease in the violet and ultraviolet region of late N-stars is not explainable in terms of a discrete molecular absorption only. The latter must be superimposed on a continuous absorption becoming appreciable near λ 4 400 and increasing shortward.

ARE POLYATOMIC MOLECULES OR RADICALS PRESENT IN LATE CARBON STARS ?

Theoretically, as was shown long ago by RUSSELL [9], polyatomic molecules like H_2O should be abundant in the latest M-stars. RUSSELL found that the abundance of H_2O in such stars is of the same order as that of the O - or N - atoms ; actually H_2O may be even more abundant than calculated by RUSSELL on account of stratification effects [10].

Similarly compounds such as $H_xC_yN_z$ and especially H_xC_y may be expected in late N-stars, the atmospheres of which contain essentially H, C, N and the neutral diatomic combinations of these atoms (H_2, CH, C_2, NH, CN, N_2).

Observationally the need for such polyatomic compounds is apparent from the fact that no known diatomic molecule can be assigned to the 4 050 group or to the unidentified green bands (Sanford bands). Certainly these two features can not be assigned to ionized molecules ; of course they can not be due to forbidden bands of neutral diatomic molecules either. All unionized diatomic combinations of H, C, N, O of high f - value have been studied thoroughly in the laboratory, and so have the likeliest diatomic combinations of these atoms with other cosmically abundant elements.

Moreover MCKELLAR has shown that the Sanford bands do not have the rotational structure which would be expected from a hydride. There seems to be no escape from the conclusion that polyatomic molecules must be present in late N-stars.

Of course chemically stable polyatomic molecules (sublimated from the nucleus) or polyatomic radicals (resulting from the photodissociation of these chemically stable molecules) are expected in cometary atmospheres. Indeed NH_2 gives rise to many cometary emissions in the visual region (α-band of ammonia) ; CO_2^+ is also observed in the tail.

Which polyatomic molecules should be expected in comets or N-stars ? In the comets only di-or triatomic combinations of H, C, N and O have been found thus far ; there is every reason to believe that the 4 050 cometary group is due to a $H_x C_y N_z O_u$ compound. In the carbon stars the 4 050 absorption must also be due to such a compound, oxygen being however excluded. The almost certain identity of the cometary and stellar 4 050 molecules should help greatly in our attempts to identify this compound.

Among the hydrocarbon molecules which may possibly be present in the latest N-stars, acetylene (C_2H_2) should be considered with special attention. Chemists generally agree that any hydrocarbon such as methane, ethane or ethylene, at the temperature of a flame transforms partly into acetylene. However acetylene has no known electronic band in the photographically observable range of stellar spectra. Should radicals such as CH_2 or C_3 have strong electronic transitions in the observable spectral range [11] we may expect to find their spectra in the N-stars or in comets.

First laboratory investigations on the 4 050 group

Herzberg [12] produced for the first time a laboratory spectrum which looked very similar to the cometary 4 050 group. This was obtained in an interrupted discharge through streaming methane. The conditions of excitation supported the assumption that the spectrum is due to CH_2. Indeed Herzberg had previously [5] shown that the cometary emission could be a $\perp$ band of a nearly symmetric top molecule like CH_2. In 1942 it was thought [13] that CH_2 had an electronic transition in the region 4 000-4 500 A. However Herzberg was cautious, and mentioned his uncertainty with regard to the emitter which, according to him, could also possibly be some other carbon compound like C_2H or CH_3.

Nevertheless the assignment to CH_2 was generally accepted, and it was thought that the CH_2 radicals in comets resulted from the photodissociation of methane. This chemically stable molecule is present as an occluded gas in meteorites and terrestrial rocks. Moreover the possibility that the CH radicals of comets result from the photodissociation of CH_2 was often envisaged. This possibility is not born out by the cometary spectra [2]. Similarly it was thought for a while that the 4 050 absorption features in the N-stars were due to CH_2 : such a radical should indeed be abundant in a late N-star if its heat of dissociation is high enough.

From Herzberg's low resolution laboratory spectrograms it was probable, but not certain, that the laboratory spectrum and the 4 050 group in comets were due to the same molecule. Moreover the assignment to CH_2 was only a suggestion which indeed had much in its favor, yet required a high resolution analysis.

Laboratory spectrograms of higher dispersion were obtained by Madame HERMAN [14] using a discharge between carbon rods in an atmosphere of hydrogen diluted with a noble gas. The presence of the 4 050 emission was also reported in an ordinary discharge through diazomethane (CH_2N_2) and ketene ($CH_2 : CO$) by GOLDFINGER, LE GOFF and LETORT [15]. No analysis of these spectra was performed.

The attempts by one of us (B. R.) to develop an intense source of 4 050 emission were successful in 1948. A hollow graphite cathode was used, with a circulation of hydrogen or of a hydrocarbon gas [16]. It was first endeavored to check the assignment to CH_2. A chemical method based on the tellurium mirror technique developed by PANETH and HODEFIZ showed that the CH_2 radical was probably not involved in the 4 050 emission. Second, a crude rotational analysis of a high resolution spectrogram indicated that the moment of inertia was much too large for CH_2. Finally the complete absence of isotopic displacement when circulating deuterium was used instead of hydrogen proved conclusively that the 4 050 molecule contained no hydrogen atom at all.

CONTRIBUTION OF THE ASTRONOMICAL DATA TO THE IDENTIFICATION OF THE 4 050 MOLECULE

The new spectroscopic observations of the late N-stars provide more convincing evidence in favor of the assignment of the laboratory emission, the 4 050 absorption in N-stars and the cometary 4 050 group to the same molecule [8]. This must be a neutral polyatomic compound containing only H, C or N. A triatomic molecule would be preferred to a more complex one having the same dissociation energy, although this should not be taken too strictly. If we assume that the new ultraviolet absorption band λ 3 790 (first band, shortward of 4 050) or the band of shortest wave length among the Sanford group, λ 4 352, belongs to the same molecule as λ 4 050 [17], the vibrational frequency ($\sim$ 1 700 K) obtained (either ω_1' or ω_1'') is very nearly the same as in the case of C_2. No such coincidence is found with a CN vibrational frequency. From the experimental conditions in which the bands were produced the presence of nitrogen atoms in the 4 050 molecule is also unlikely. It has moreover been shown previously that the 4 050 molecule contains no hydrogen.

The best guess for a triatomic molecule would thus be the triatomic carbon C_3 compound (a suggested name : carbozon) [18].

If one tries to classify the succession of absorption features observed in N-stars shortward of λ 4 050 as a K-rotational series [19] corresponding to the smallest moment of inertia of a bent C_3 molecule, it is found that the moment of inertia about the top axis is very small, of the order of 0.33×10^{-40} g. cm², i. e. even smaller than that of hydrogen (0.46×10^{-40}). Hence in this assumption the apex angle of the bent molecule would be extremely close to 180°. This is unlikely : the structure near 4 050 observed in comets and N-stars must most probably be of vibrational origin. Actually the belief has been expressed that the C_3 molecule should rather be linear [20].

RECENT INVESTIGATIONS ON THE IDENTIFICATION OF THE 4 050 MOLECULE

DOUGLAS [21] pursued the analysis of the 4 050 band further. He confirmed that hydrogen is not present in the 4 050 molecule. Replacing C^{12} by a mixture of C^{12} and C^{13} he found six R–heads ; such a result may possibly be understood if the emitter is a triatomic C_3 molecule, in agreement with the astronomical evidence. For the main transition near λ 4 050 a $\Sigma \rightarrow \Pi$ transition, in which every other rotational line is missing (assuming a linear C_3 molecule, and since C^{12} has no nuclear spin) leads to a reasonable internuclear distance on the basis of the P-and Q-branches. However the values for D' and D'' are rather large, the Λ doubling does not vary as $J\ (J + 1)$, and it is large even for $J = 0$. Moreover DOUGLAS found it difficult to interpret the structure in the R-branch where the lines have a rather irregular spacing - and intensity distribution. DOUGLAS concludes that the molecule contains more than one C–atom and that the assignment to C_3 has merit. The bands other than 4 050 are very complex and their analysis was not attempted.

Two crucial experiments have been suggested by DOUGLAS and would help greatly in determining the emitter : the excitation of the bands at low temperature (simplifying the rotational structure) and the use of a pure C^{13} source (in which case a linear C_3 molecule would give twice as many lines as with C^{12}).

DOUGLAS did not attempt a vibrational analysis of the laboratory spectrum. Possibly the following classification (table 1) may be suggested for the emission bands found in the laboratory. The data in this table refer to spectra taken with medium dispersion and are mean values selected from the lists given by R. HERMAN [14] and R. ÉTIENNE [16].

TABLE 1

TENTATIVE VIBRATIONAL CLASSIFICATION OF THE LABORATORY EMISSION BANDS

	0′		1′		2′
	—		—		—
0,0,0″	4 050 (10)		4 018 (6)		3 991 (2)
	(24 685)	196	(24 881)	168	(25 049)
1,1,0″	4 073 (5)		4 041 (5)		4 013 (2)
	(24 545)	194	(24 739)	173	(24 912)
2,2,0″	4 099 (1)		4 067 (1)		4 038 (4)
	(24 389)	192	(24 581)	177	(24 758)

This classification would indicate a frequency of about 200 K in the excited electronic state. Whether this low frequency and one of about 1 700 K may belong to excited C_3 should be examined.

Actually a vibrational classification may appear easier on the basis of the cometary emissions which are sharper and clearer than the laboratory bands (lower rotational temperature in comets). However another difficulty may arise in this case if the 4 050 group is excited by resonance-fluorescence as are the CN, OH, CH,... bands. The solar absorption lines may affect the profile of cometary bands ; the $\Delta\sigma$'s may thus be perturbed, and the classification may become somewhat uncertain. This difficulty is probably not serious since comets having different radial velocities relative to the sun (i. e. different Doppler shifts of the Fraunhofer lines) do not seem to have different profiles for the 4 050 group. A tentative classification is suggested in Table 2 which includes almost all the observed emissions of the cometary 4 050 group.

TABLE 2

TENTATIVE VIBRATIONAL CLASSIFICATION OF THE COMETARY BANDS

	$0'$	$1'$	$2'$	$3'$	$4'$
$0,0,0''$	4 051.6 (7) (24 674.7) 197.6	4 019.4 (4) (24 872.3) 167.0	3 992.6 (4) (25 039.3) 152.7	[3 968.4 (1)] [25 192.0]	
$1,1,0''$	4 074.4 (4) (24 536.6) 196.1	4 042.1 (5) (24 732.7) 178.0	4 013.2 (4) (24 910.7) 162.5	[3 987.2 (3)] [25 073.2] 149.9	[3 963.5(1^+)] [25 223.1]
$2,2,0''$	4 099.5 (2) (24 386.4) 186.4	4 068.4 (2^+) (24 572.8) 175.2	4 039.6 (5) (24 748.0) 162.7	4 013.2 (bl) (24 910.7)	

A vibrational classification of the absorption bands in N-stars can hardly be performed, on account of blends and low resolution on the available spectrograms. However the progression 4 052.8 — 4 019.8 — 3 994.7 is clear ; the $\Delta\sigma$'s (202 and 156 kaysers) are in reasonably good agreement with the cometary and laboratory values. The second progression beginning with 4 077 is weaker and difficult to disentangle. The third progression is very weak although λ 4 100 is definitely present. Absorption features shortward of λ 3 960 would correspond to higher v'-values.

If this scheme is correct, the vibrational intensity distribution within the cometary 4 050 group would be somewhat similar to that in the cometary Swan bands. It would indicate that there are appreciable populations on the levels $v'' > 0$, hence that the 4 050 molecule has probably no permitted pure vibrational spectrum, i. e. no permanent dipole. Actually the vibrational temperature may be lower in the N-stars (where it has a meaning) than in the comets (where it is purely artificial since collisions are rare). The intensity ratio of λ 4 077 and λ 4 053 may be smaller in absorption in N-stars than in emission in comets. It may even be smaller in N-stars than in laboratory absorption (see further on), if the laboratory temperature happens to be higher than that of the 4 050 molecules in an N-star.

The absorption peak 4 052.8 in N-stars as well as the width of the 4 052.8 band indicate a low temperature, probably somewhere between 1 000 and 2 000° K. However spectrograms of N-stars with a higher resolution are required to settle this matter.

RELATIONS TO PHENOMENA IN DISCHARGES, FLAMES, PYROLYSIS AND PHOTOLYSIS

While the assignment of the 4 050 group to the C_3 molecule appears promising on the basis of astronomical and experimental evidence it can not be considered as demonstrated yet. Accordingly it is useful to review the data on the excitation conditions, always keeping in mind the main astronomical problems : *a*) the 4 050 group itself, and its behavior ; *b*) the continuous absorption in the N-stars, shortward of λ 4 400. Recent investigations in the London and Cambridge laboratories on flames, pyrolysis and photolysis as well as the work in Liège with the hollow cathode have a direct bearing on these two astronomical problems.

A) *Hollow cathode* [16]. — When H_2, D_2 or HD is circulated in the hollow cathode the 4 050 emission takes place only when the discharge is accompanied by tiny bright " sparks " (incandescent carbon particles !) and by the resulting formation of soot. When an organic compound (methane, benzene, toluene, cyclohexane,...) is circulated the 4 050 emission may or may not be accompanied by " sparks ", but is always accompanied by formation of solid carbon. If the cathode gets hot the intensity of 4 050 decreases, and so does the formation of soot. Hydrogen—free or bound—is required for the production of the 4 050 molecule although the latter does not contain the hydrogen atom. Summarizing : the 4 050 molecule is formed by interaction of hydrogen with graphite or by transformation of organic molecules ; it is accompanied by the formation of carbon black.

B) *Flames.* — 4 050 emission was first found in a flame by DURIE [22] in the reaction of fluorine with organic compounds, diluted to a variable extent by hydrogen. 4 050 appears at a stage when there is still high continuous luminosity (i. e. considerable formation of soot) and strong C_2 emission, and when the CH band begins to appear. When the concentration of H_2 increases 4 050 disappears, together with the continuous emission from the carbon.

Instead of adding H_2 the vapor pressure of the compound may simply be increased. However the molecule must contain hydrogen in order to give rise to 4 050 emission : f. ex. H_2 has to be added if CCl_4 is used.

DURIE also obtains 4 050 in the reaction of F_2 with organic halogen compounds such as chloroform or trichlorethylene, when C_2 is still intense, CH beginning to appear, and there is important formation of soot.

DURIE's results are similar to those obtained with the hollow cathode : hydrogen (bound or free) is required for the 4 050 emission, which is moreover accompanied by the formation of carbon black.

More recently GAYDON and WOLFHARD [23] have observed 4 050 emission in the reaction of hydrogen atoms or OH radicals with hydrocarbons (acetylene, methyl alcohol,...) or CCl_4 in their " atomic flames ".

4 050 emission has also been found in the flames of rocket jets using various fuels [24].

C) *Photolysis.* — NORRISH, PORTER and THRUSH [25] observed 4 051 in absorption in an acetylene-oxygen explosion caused by a photoflash ; λ 4 072 has also been found in absorption, actually more strongly than 4 051 [26]. The temperature created by the flash in the case when 4 051 and 4 072 were observed is of the order of 3 000°. The 4 051 absorption is accompanied by formation of solid carbon. There is a striking parallelism between the 4 051 intensity and the carbon formation when the concentration of C_2H_2 relative to O_2 varies [26].

The fact that the intensity ratio of the 4 072 and 4 051 absorptions is higher in PORTER's experiment than in the N-stars may be due to the higher temperature created by the photoflash. However this point requires further study ; no " reversal effect " may be invoked in this case [26].

D) *The formation of solid carbon particles.* — The formation of soot in photochemical decomposition has been studied extensively by NORRISH, PORTER and collaborators [26], [27] in the case of ketene ; the important role of acetylene was particularly stressed.

The carbon formation in flames and in pyrolysis was reviewed and further investigated by PARKER and WOLFHARD [28]. The problem of soot formation has considerable industrial importance, hence has been the object of numerous investigations. In the pyrolysis of organic vapors PARKER and WOLFHARD noticed an absorption continuum covering the ultraviolet and extending the farther toward the visible the greater the number of C-atoms relative to H and the higher the temperature. In the pyrolysis of acetylene the absorption continuum extends to λ 4 500 at 800° K. This continuum may be explained in different ways ; it is rather tempting to assign it simply to absorption by carbon particles or by droplets. It is known that the diameter of the soot particles, as determined with the electron microscope, is of the order of 200 A (between 100 and 1 000 A) ; electron diffraction gives a smaller figure (of the order of 20 A), but this may be affected by irregularities in the shape of the carbon grains.

The whole problem of the formation of carbon black is still in an uncertain state [29]. In the diffusion flames WOLFHARD finds that the carbon formation can not be due to polymerization and condensation of C_2 molecules : solid carbon is formed in a region of the diffusion flames different from that where the C_2 emission originates. In the pyrolysis of organic vapors the carbon formation is not accompanied by absorption in the Swan bands. In premixed flames the carbon formation must be due to a very rapid chain mechanism (GAYDON). NORRISH expresses the view that carbon atoms — the presence of which is not known in flash photolysis, but is possible — may combine and build C_2, C_3,.., and eventually solid carbon. However if this were the case it appears strange that there is no soot formation in a cyanogen flame which may also contain C-atoms (GAYDON). Porter stresses the experimental fact that there is no correlation between the C_2 bands and carbon formation in premixed flames. Since any hydrocarbon would partly break down into acetylene, PORTER imagines a chain built up by acetylene molecules. The hydrogen atoms would soon be partly thrown out of such a chain : indeed one always finds some hydrogen (order of 10 per cent) left in carbon black. According to PORTER acetylene is the only hydrocarbon which should be considered; the possible effect of other radicals, added to the C_2H_2 molecule, such as was tentatively suggested by GORDON, is not favored by PORTER.

Whatever the actual mechanism of formation of solid carbon particles may be, it is apparent that the 4 050 molecule is related to that formation in discharges, flames and photolysis. This molecule must be an intermediary compound in the formation of carbon black [29]. At this point of view C_3 is a reasonable supposition ; however from the purely physical standpoint, other carbon molecules, such as C_6, may also be possible. The 4 050 molecule is also directly related to the continuous ultraviolet absorption.

THE N-STARS

The atmosphere of a late N-star is composed of H, H_2, C, CH, C_2, N, NH, CN, N_2, plus a few heavier atoms and diatomic molecules of low abundances ; stable polyatomic compounds such as acetylene, and polyatomic radicals should be expected. The conditions are favorable for pyrolysis, and possibly even for photolysis. That C_3 molecules may thus be formed is reasonable. Moreover the conditions are right for the appearance of an ultraviolet absorption continuum, such as observed in the laboratory in the pyrolysis of acetylene.

Thus the atmosphere of a late N-star should be pictured as containing, probably on its outskirts, solid carbon particles. There is some kind of smoke veil around the star causing a reddening by absorption of the ultraviolet.

A veiling effect by smoke has been occasionally envisaged to interpret various astronomical phenomena, even in the case of novae. A late N-star would be a striking example. The smoke veil would vary in variable N-stars.

THE COMETS

In the hollow cathode 4 050 molecules and carbon particles are formed by impact of hydrogen on the graphite walls. In flames H-atoms plus organic molecules produce 4 050 emissions. In all the 4 050 sources free or bound hydrogen is required, although the 4 050 molecule itself does not contain hydrogen.

Could the 4 050 molecules in comets be formed by the impact of the solar protons on the ices of carbon compounds of the nuclei (frozen acetylene [30] or methane, possibly in the form of solid hydrates), or on the sublimated molecules containing carbon atoms lying close to the solids ?

Of course the formation of cometary C_3 molecules should theoretically not require necessarily the impact of hydrogen on carbon compounds. We may think of the possible photodissociation of sublimated $C_{3+x}H_yZ$ molecules. Or we may also envisage chemical reactions between atoms, molecules and radicals, close to the icy nucleus where sublimation takes place and where the density may be high enough to make reactions possible.

Nevertheless it seems useful to pursue the working hypothesis of the formation of 4 050 molecules by the impact of solar protons on the comet, on account of the peculiar behavior of the 4 050 molecules in comets. Many authors have, at one time or another, considered the possibility that a cometary atmosphere may be formed by the impact of solar electrons or particles. In the present case only one specific kind of cometary molecules is envisaged.

The 4 050 bands " more than any others show the variation in intensity in different comets regardless of the heliocentric distance " (N. T. BOBROVNIKOFF [31]). Moreover, as has been mentioned before, the behavior of 4 050 with respect to heliocentric distance differs from that of CH, C_2 or CN. In a general way its intensity does not increase rapidly with decreasing r, so that it decreases in intensity relative to CH, C_2 or CN (especially CH and C_2) when the comet comes closer to the sun. For molecules such as CH or C_2 the rapid intensity increase with decreasing r is due at least partly to the rapid sublimation of the heated ices [32]. If 4 050 molecules are built by impact of solar protons on the solids their rate of formation should only vary like r^{-2} while the abundances of the other molecules depend on the vapor pressures which are steeper functions of r.

Could enough 4 050 molecules be built by such a collisional process ? According to BIERMANN [33] the number of solar protons (or electrons) colliding with a comet nucleus, or with the gaseous layer of chemically stable molecules covering the solid, may be taken as from 10^{11} to 10^{12} cm^{-2} sec^{-1} at one astronomical unit. In case of a " magnetic storm " the figure would be raised to 10^{13} or 10^{14} cm^{-2} sec^{-1}.

A similar or somewhat higher figure is obtained from MEINEL'S observation of the solar protons in aurorae. If we adopt a diameter of one kilometer for the comet nucleus the number of proton hits on the solid is from 3×10^{21} to 3×10^{22} sec^{-1}. If reactions of the protons with the overlying stable molecules are considered the previous figure would be increased slightly. Let p be the probability that a proton hit on the solid or on one of the sublimated molecules gives a 4 050 molecule. If τ seconds is the average life of a 4 050 molecule in the field of solar radiation before it is photodissociated or photoionized the " 4 050 head " of the comet will contain from $3 \times 10^{21} \times p\tau$ to $3 \times 10^{22} \times p\tau$ 4 050 molecules. We have no idea of the values of p and τ. If we assume τ to be the same as for CN it would be of the order of 10^5 seconds (the normal extension of a CN-head at 1 A. U. is greater than 10^5 km ; the velocity of CN-radicals is of the order of 1 km/sec ; the 4 050 head is much smaller, probably on account of a smaller velocity of the 4 050 molecules). Let us assume that the 4 050 head of the comet has a diameter of 2 000 km. The average density in 4 050 molecules will then be from 75 p to 750 p per cm^3. If p is of the order of 0.1 the density of 4 050 molecules would probably be high enough to satisfy the observations. The precarious character of the assumptions on τ and p, and even on the radii of the nucleus and of the 4 050 head is fully realized. The only conclusion which we wish to draw is that the production of 4 050 cometary molecules in this fashion is not excluded altogether.

Should this mechanism be actually operative we would expect to find a correlation between the intensity of the 4 050 cometary emission and the solar activity or the sudden brightening of comets [34]. An additional way of exploring the solar field via " cometary aurorae " would thus be provided ! We plan to examine whether such a correlation exists in the case of comets for which sufficient series of spectra are available.

One may wonder whether the colliding electrons and protons could not excite the 4 050 molecules as well as create them. This appears rather unlikely on the basis of BIERMANN's calculations [35]. Yet a careful re-examination of the 4 050 profiles in different comets with different radial velocities may not be altogether fruitless. From the general appearance of the 4 050 group it seems that its profile does not vary appreciably with the radial velocity of the comet relative to the sun [36]. On the contrary the CN, OH and CH profiles vary [37]. The effect of the Fraunhofer lines on the profile of the 4 050 group may of course happen to be minor [38]. Nevertheless the possibility of an excitation other than by resonance-fluorescence should not be altogether excluded.

If 4 050 emission is excited only at the time of the creation of the molecule by impact the corresponding contribution would not account for the observed emission over a fairly large volume. On the other hand one does not see why electrons or protons would excite 4 050 molecules and not the other usual radicals which do not require a higher amount of excitation. As is demonstrated by the study of the resonance-fluorescence effects the spectra of OH, CH, CN (violet), etc... are all excited purely by absorption of solar radiation and resonance-fluorescence. If photodissociation or collision contributes to the emission it can only be for an extremely small fraction of the resonance-fluorescence for OH, CH, CN, etc.... Yet the fact remains that one cometary emission, the red CN system, which like 4 050 is concentrated in the central part of the head, does not appear explainable by the fluorescence mechanism. Possibly the relative intensities of the red CN system and of 4 050 would be profitably compared.

One of the authors (P. S.) prepared his share of this paper while residing at the University of California as visiting lecturer in the Berkeley Astronomy Department. He wishes to thank Dr. STRUVE, Chairman of the Department, for his cordial hospitality and for his interest in this work.

Manuscrit reçu le 17 février 1953.

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[3] See reference (2) for comet 1948 *l*. The diffuse character of the 4 050 emission had been observed in previous comets, f. ex. in 1911 V (Brooks).

[4] This appears clearly in many comets, f. ex. in 1893 III (Rordame), 1894 II (Gale), 1907 IV (Daniel), 1941 I (Cunningham), 1948 *l*. (bright Southern).

[5] G. HERZBERG, *Rev. Mod. Physics*, **14**, 1942, 195 ; P. SWINGS, *Pub. A. S. P.*, **54**, 1943, 123 and *Rev. Mod. Physics*, **14**, 1942, 190. For discussions of the old observations of 4 050 and of the first identification attempts, see N. T. BOBROVNIKOFF, *Ap. J.*, **73**, 1931, 61 ; P. SWINGS, C. T. ELVEY and H. W. BABCOCK, *Ibid.*, **94**, 1941, 320..

[6] G. A. SHAJN and O. STRUVE, *Ap. J.*, **106**, 1947, 86.

[7] A. MCKELLAR, reference (1) ; P. SWINGS and MCKELLAR, *Ap. J.*, **108**, 1948, 458.

[8] P. SWINGS, A. MCKELLAR and K. N. RAO, Paper presented at *The* 1952 *Meeting of the I. A. U. in Rome* (joint session of commissions 27 and 29). A detailed paper is in preparation.

[9] H. N. RUSSELL, *Ap. J.*, **79**, 1934, 317.

[10] P. SWINGS, *Pub. A. S. P.*, **54**, 1942, 232.

[11] From the intensity of the 4 050 group in comets and N-stars it is expected that the f-value of the involved electronic transition is fairly high, whatever the molecule may be.

[12] G. HERZBERG, *Ap. J.*, **96**, 1942, 314.

[13] According to recent calculations by J. DUCHESNE the electronic transition of CH_2 is in the far ultraviolet, probably near λ 1 800 (privation communication, November 1952).

[14] R. HERMAN, *C. R.*, Paris, **223**, 1946, 281.

[15] P. GOLDFINGER, P. LE GOFF et M. LETORT, *C. R.*, Paris, **227**, 1948, 632.

[16] A. MONFILS and B. ROSEN, *Nature*, **164**, 1949, 713 and *Liège Publication*, in-4°, n° 27, 1950 ; R. ÉTIENNE, *Thesis*, *Liège*, 1950 (unpublished) ; R. ÉTIENNE, P. LE GOFF et B. ROSEN, *Liège Publication*, in-4°, n° 29, 1951 ; B. ROSEN, paper presented at *The Liège Symposium on « La physique des Comètes »*, September 1952, *Mém. Soc. Roy. Liège*, **13**, 1953, 187.

[17] There is some astronomical evidence, although not conclusive, in favor of assigning the unidentified green bands of N-stars to the same molecule as 4 050 (reference 8). From the general appearance of the new ultraviolet bands of N-stars one is tempted to assign these also to the 4 050 molecule. Thus far there is no laboratory evidence based on emission spectra, favoring such a common origin, but this possibility is now being investigated more thoroughly in our laboratory.

[18] Announced by one of us (P. S.) in 1950 in unpublished lectures, and in « La physico-chimie des comètes », Conférence du Palais de la Découverte, Paris, April 1951. The suggested name « carbozon » may not be quite satisfactory since ozon is a bent molecule while the geometrical structure of C_3 is not known as yet.

[19] This is the same procedure as that followed by Herzberg in the CH_2 - assumption, reference 5.

[20] Private communication from Dr. de Heer (Columbus, Ohio, March 1951).

[21] A. E. Douglas, *Ap. J.*, **114**, 1951, 466.

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[23] A. G. Gaydon and H. G. Wolfhard, *P. R. S.*, London, A, **213**, 1952, 366.

[24] Private communication from Dr. Moe (Aerojet Corporation, December 1952).

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[28] W. G. Parker and H. G. Wolfhard, *Jour. Chem. Soc.*, 1950, 2038.

[29] B. Rosen (ref. 16, 1953) ; Symposium and discussion session on the spectroscopy of combustion, *American Physical Society*, 316 *th meeting*, December 26-27, 1952, unpublished.

[30] The melting point of acetylene (— 81.8° C) is nearly the same as that of ammonia (— 77.7° C) ; while that of methane is much lower (— 184° C). However if these compounds are present as solid hydrates or similar composite solids their vapor pressures would be of the same order (A. Delsemme et P. Swings, *Ann. d'Aph.*, **15**, 1952, 1). The CH-radicals may result from the photodissociation of acetylene molecules sublimated from the ices of the nucleus, as well as from the photodissociation of the commonly considered methane.

[31] N. T. Bobrovnikoff, in *Astrophysics*, edited by A. J. Hynek, p. 346.

[32] As was shown by K. Wurm (*Mitt. Hamburger Sternw.*, **8**, 1943, 57), the problem is actually more complicated than in the present paper. However a qualitative treatment suffices here.

[33] L. Biermann, *Zs. f. Ap.*, **29**, 1951, 274. Biermann's figures for the number of solar protons may be too high (Whipple, private communication, march 1953).

[34] L. Biermann, *Zs. f. Naturforschung*, 7a, 1952, 127 ; also paper to *The Liège symposium on « La Physique des Comètes »*, September 1952, *Mém. Soc. Roy. Sc. Liège*, **13**, 1953, 291.

[35] L. Biermann, first reference 34, pp. 135-136 (« Ergänzende Bemerkungen »).

[36] At least there are very few trustworthy references to such differences. One was mentioned by C. Fehrenbach (*C. R.*, Paris, **227**, 1948, 519), who stated that λ 4 013 and λ 4 067 were anomalously intense in 1948 g.

[37] This is due to the Doppler shift of the Fraunhofer lines in the solar radiation which excites the CN, OH and CH bands by resonance-fluorescence.

[38] It would be possible to differentiate between resonance-fluorescence excitation and other mechanisms (such as photodissociation, collision or chemical reaction) by measuring the amount of polarization of the 4 050 emission.