

given under (2) and (3) agree very well with observations by the author, who had noticed long ago the differences in photometric behaviour between the slim bright tail-comets and the round faint condensed objects. With some certainty one can tell from the mere appearance of a comet in a telescope whether it is an old or a new object.

#### 9. PROPOSALS FOR FUTURE RESEARCH

The preceding remarks were made mainly in order to stimulate future observations of comets. Even if spectrograms of objects which are often very faint encounter difficulties, exposures with suitable filters should provide important insight into the physical structure of the heads and tails. One should aim at obtaining an extensive series of short exposures of the photographically bright tails at rapid intervals with large reflecting telescopes, in order to be able to study their structure and the movement of matter inside the tails. Finally, photoelectric photometry will find a field of application which has until now only been explored with very primitive means.

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## The Spectra of the Comets

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#### SUMMARY

The Introduction deals with the essential information on the nucleus, the coma, and the tail of comets, which may be obtained by direct photography, photometry, and polarization techniques; the need for "monochromatic" observations is emphasized. It is followed by a description of the emission spectrum of the coma (from the OH emission near  $\lambda 3100$  to the red CN band near  $\lambda 8100$ ) and by that of the spectrum of the tail in the ultraviolet and photographic regions, with emphasis on the recently discovered bands. The complex profile of the emission bands is shown to be due to a resonance fluorescence excitation, account being taken of the absorption lines of the exciting solar radiation; other possible excitation mechanisms are briefly mentioned. The probable assignment of the  $\lambda 4050$  group to the tricarbon molecule and its consequences are discussed. The paper ends with physical considerations on the still unidentified emissions, on desirable physical investigations, on the parent molecules, and the production and evolution of cometary atmospheres, and on the densities and the extent of molecules in the cometary head.

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#### 1. INTRODUCTION

PROFESSOR STRATTON's thorough work was an inspiration to most beginners in the field of spectroscopy a quarter of a century ago. For this he deserves the deep gratitude of the astrophysicists of my generation. I wish to add my personal heartfelt thanks to Professor STRATTON for all the encouragement he has generously given me. It is with pride and joy that I dedicate this paper to our dear friend on his Jubilee.

A comet consists essentially of three parts: a nucleus of small dimension, of the order of a few kilometres or less; a coma (or head) surrounding the nucleus and extending to hundreds of thousands of kilometres; and a tail which usually is directed away from the Sun and may have a length of millions of kilometres [1]. Except when the comets pass very close to the Earth the nuclei appear star-like in a large telescope. The diameters of these nuclei have seldom been measured and then only

in a rather crude fashion. For comets 1927 VII (Pons-Winnecke) and 1930 VI (Schwassmann-Wachmann), BALDET [2] found diameters of approximately 400 m; the geocentric distances of these comets were respectively  $5.8 \times 10^6$  km and  $8.4 \times 10^6$  km only at the times of the observations. Of course, BALDET's observations do not exclude the presence of fainter nuclei in addition to the ones he measured. Actually double and multiple nuclei are often observed; the breaking of a comet into two or more comets [3] is not infrequent, a recent case having been the bright southern comet 1947n, for which spectra of the two components were obtained [4]. The nucleus has a very small mass; passage of a comet near a planet has no appreciable influence on the latter or on its satellites even when the comet's orbit is considerably affected. The structure of the nuclei has been discussed in several recent papers, for example, by VORONTSOV-VELYAMINOV [5] and by LEVIN [6].

The size and appearance of the coma depend on the molecular band in which the comet is observed. As will be seen later, different molecules extend to quite different distances from the nucleus; moreover, certain features like jets may have a characteristic spectrum. A gaseous coma is much smaller if photographed near  $\lambda 4050$  or  $\lambda 6300$  than if photographed near  $\lambda 3888$  or  $\lambda 5150$  or  $\lambda 4735$ . Actually the head of a comet may be the superposition of many features, jets, halos, and envelopes, as well as of an indefinite atmosphere. In general a photograph of the coma in the red will appear smaller than one in the green or the near ultra-violet. Isophotes in the red and blue region have recently been obtained by K. M. YOSS [7] for the periodic Comet Schaumasse (1951I). While the separation of the characteristic emissions could still be greatly improved, the observations by YOSS reveal striking differences between the blue and red images. VORONTSOV-VELYAMINOV [8] has determined the decrease in density of  $C_2$  and CN with distance from the centre of the nucleus, on the basis of photographs of the head of 1943 I (WHIPPLE-FEDTKE). The first attempts at photographing comets through filters go as far back as 1907 (G. A. TIKHOV).

As for the tail, various sizes and aspects may be encountered, from a set of sharp streamers to a diffuse cloudy appearance. The latest classification of cometary tails and heads is that of S. V. ORLOV [9]. Just as in the case of the head, photographs of the tail taken in different spectral regions, corresponding to bands of specific molecules or to the continuum, may be different. T. CLAASEN found that the tail may appear sometimes in the ultra-violet and not in the red (Comet 1941 I, CUNNINGHAM on 29th December, 1940), or vice versa (Comet 1942 IV WHIPPLE, on 12th and 13th March, 1942).

The data on the trajectories, aspects, and internal motions of the comets are essential to the understanding of these objects. Despite the large amount of accumulated data on the appearances of comets and on the motions within the head and tail we do not as yet possess enough information for a thorough discussion of many dynamical aspects of the formation and evolution of the heads and tails [11]. The first theory of cometary forms goes back to BESSEL's treatise on Comet 1835 III (HALLEY [12]). This was developed by BREDICHIN and by several Russian astronomers. Contributions are also due to A. KOPFF and to A. S. EDDINGTON [13]. Indeed, it may almost be said that we have not gone far beyond EDDINGTON's classical "fountain model" study of the transitory envelopes of Comet 1908 III (MOREHOUSE), although recent contributions by K. WURM [14] to the structure of the  $CO^+$  tails and of A. D. FOKKER [15] to the fountain model itself have brought new light to the problem. On account of the complexity of the radiation emitted by the different

regions of a comet it appears that our crucial need at present is for well-planned simultaneous photographic and spectrographic observations. Inasmuch as possible the photographic observations should be made with filters transmitting only physically well defined radiations.

Similarly it may be stated that the photometry of comets, despite the many thousands of published magnitudes, is still in a state of infancy as far as its contribution to the physical understanding of cometary mechanisms is concerned. As will be seen in detail later on, the light emitted by a comet is the sum of a continuous solar spectrum and of a number of molecular and atomic radiations. These constituents of the light originate in different parts of the comets. The solar continuum comes mainly from the nucleus, while certain bands appear near the nucleus, others in remote parts of the head, and still others in the tail, either near to or far from the nucleus. Sometimes striking differences in colour (*i.e.* in spectrum) appear in various details of a coma. While the comet travels around the Sun each constituent of the light varies in its own way with heliocentric distance. The observed magnitude, if it is not carefully limited to specific spectral ranges by using adequate filters, is a summation over all the contributions. It is obvious that such an integrated brightness has only a limited meaning. The colour index is known to vary greatly as a function of the heliocentric distance or even suddenly, as was shown already by TIKHOV in 1908, and more recently by KNOX-SHAW (Comet 1910 II, HALLEY), KUKARKIN (1930 III, WILK), VAN SCHEWICK (Comet 1937 V, FINSLER), and L. GIALANELLA (various comets from 1939 to 1942). Indeed the colour may differ from one detail of the head to another, and fluctuate rather rapidly. An effort should be made in the direction of "monochromatic photometry": accurate data, obtained with photoelectric receivers, on the variation with heliocentric distance of the emission by a specific molecule or in the continuum would bring most valuable information. An effort in this direction is presently being made at the Leiden Observatory [16], and other astronomical institutions are contemplating similar work.

Poor as they are, the integrated brightnesses have already led to interesting conclusions. Recent refinements in the photographic photometry by BALDET [17] and in the visual photometry by MERTON [18] will still improve these data. It is to be hoped that adequate filters will eventually be combined. It is on the basis of the presently available crude estimations of brightnesses that BOBROVNIKOFF, LEVIN, VSEKHSVYATSKY, LINK, BOUŠKA, VANÝSEK, ŠVESTKA, and others discussed the variation of the brightness as a function of heliocentric distance, for different comets, at different returns (if periodic), and before and after perihelion passage. The most thorough discussion is that by BOBROVNIKOFF [19]. If the variation is represented

by a formula  $I = \frac{I_0}{\rho^{2+n}}$  ( $r$  = heliocentric distance,  $\rho$  = geocentric distance), a wide range in values of  $I_0$  and of  $n$  is found for different comets [20]. Actually it is clear from the above that the notion of the absolute magnitude  $I_0$  is highly artificial if based on integrated brightnesses. As for  $n$ , this should indeed vary erratically when it results from an integration over spectral ranges of different physical significance. These old magnitudes, crude as they are, have greatly helped OORT and SCHMIDT in their beautiful comparison of "old" and "new" comets and in their discussion of the origin of these objects.

Comets may differ greatly in the amount of gas which they generate. Let us designate by  $\Delta m$  the difference in magnitude between the comet as a whole and the

nucleus. It is found that  $\Delta m$  depends essentially on the distance and is usually a maximum at perihelion or somewhat later. However,  $\Delta m$  is sometimes unusually large. Sometimes, too, there is practically no atmosphere (example: Comet 1913 III, NEUJMIN, period 17.9 years,  $\Delta m \leq 0.5$  m). Comets may appear stellar at certain times and have a coma at some other time (example: Comet 1925 II, SCHWASSMANN-WACHMANN).

It is obvious that physical studies on comets require the knowledge of the orbit data: helio- and geocentric distances, perihelion distances, periods, radial velocities relative to the Sun, departures from expected motion (as in the case of ENCKE's comet, and others). Important arguments in favour of WHIPPLE's model of the comet nucleus which will be mentioned later are based on the acceleration or deceleration of certain orbits. Intensity distribution within bands can be interpreted only by taking into account the radial velocities. In this case, as in most others, astrophysics cannot be separated from astronomy and celestial mechanics.

The polarization of the light of comets was observed as early as 1819 by ARAGO; other observations were made by SECCHI, 1861-7, A. W. WRIGHT (1881), DANJON (1927). The latest measurements which were conducted a few years ago by ÖHMAN [21] had their special usefulness. Their theoretical basis is the following. For transitions such as  $\Sigma \rightarrow \Sigma$ ,  $\Pi \rightarrow \Pi$  the total polarization of fluorescence bands excited by unpolarized light should be equal to 7.6 per cent. For a transition such as  $\Sigma \rightarrow \Pi$ , involving a change in  $\Lambda$ , the polarization should be 19 per cent. If the values obtained for cometary bands should be found to be lower than these values, this would indicate the presence of a mechanism other than fluorescence, such as excitation by collisions. ÖHMAN's observations gave weight to the assumption that the emission of various cometary radiations is due to a fluorescence mechanism excited by solar radiation. From all the observations it is apparent that the amount of polarization in comets and its distribution show fluctuations just as the brightness and colour.

The most important data on cometary physics gathered in recent years result from the spectroscopic observations combined with the photometric and geometric data. The first visual observation of a comet spectrum was that of comet 1864 II (TEMPEL) by DONATI in 1864; the first slit spectrogram was photographed in June, 1881. Since then the spectra of about seventy comets have been observed photographically [22].

The essential object of this paper is to describe the present status of our knowledge of the cometary spectra. Topics which are closely related to the spectra will also be mentioned briefly, but the general field of cometary physics will not be discussed in detail.\* Since the surface brightness of comets is in most cases very weak spectrographs of high luminosity must be used. One of the most efficient combinations employing a plane grating and a solid Schmidt camera has been recently discussed by T. L. PAGE [23]; several of the new results described later on were obtained with this instrument attached at the prime focus of the 82 in. reflector at the McDonald Observatory. Suppose that we photograph the slit spectrum of a comet while guiding as carefully as possible on the nucleus (or on the brightest central part of the coma). Each point along the length of the slit—hence along the spectral line, since astronomical spectrographs should always be stigmatic—will correspond to a given region of

\* See also M. BEYER's report "On the present situation in cometary research" in *Vistas in Astronomy*, pp. 949-953, 1956, being the preceding article in this volume.

the comet. The slit may even be oriented in the direction of the tail, thus giving us part of the tail spectrum in addition to the coma and nucleus. The nucleus will give us a very narrow spectrum identical to that of the Sun with the usual solar absorption lines: the nucleus is a solid or a set of solids which simply reflects solar radiation. On either side of the narrow solar continuum of the nucleus the spectrum reveals emissions extending to a variety of distances from the nuclear continuum. On these discrete emissions a solar continuum is often superposed, showing that the coma may sometimes contain solid particles in addition to gases. If the slit covers the tail, the corresponding characteristic emissions are also observed, extending to various distances. This matter of extension will be discussed later on. The spectra of different comets observed at the same heliocentric distance may differ considerably in the intensity ratio, either of the continuum to the emission bands, or of different bands relative to each other. Moreover the spectrum varies considerably with the distance from the Sun. It is largely continuous at distances greater than 2.5 A.U.

It is obvious that slitless spectrograms give the whole distribution of the different emissions within the comet. However, only slit spectrograms were used in the descriptions which follow, and these require a fairly high resolution [24].

## 2. DESCRIPTION OF THE SPECTRUM OF THE HEAD

At its ultra-violet end a comet spectrum shows the (0, 0) band of the  $A^2\Sigma^+ \rightarrow X^2\Pi_i$  transition of OH [25]. However, the aspect of the OH band in comets differs radically from any laboratory source, even at a low temperature. The (0, 0) band of OH is easily obtained in emission in the laboratory, and it may also be obtained in absorption without too much difficulty. It has four heads, two *R* and two *Q*; on laboratory spectra the most clearly defined head is that of *R*<sub>2</sub> at  $\lambda 3064$ . However, in comets the OH band consists only of very few sharp lines. For example, eleven lines (seven fairly strong) measured in Comet 1941 I (CUNNINGHAM) had wavelengths from  $\lambda 3078.5$  to  $\lambda 3106.0$ ; in Comet 1947 *k* (BESTER), eight lines were measured, from  $\lambda 3081.5$  to  $\lambda 3107$  [26]. The intensity distributions among the lines were entirely different in 1941 I and 1947 *k*, and did not resemble any laboratory source. The wavelength of the individual cometary lines of OH coincide perfectly with the laboratory values for small rotational quantum numbers (low temperature source!), but the relative intensities differ radically. This remarkable behaviour of OH repeats itself for all other molecular bands, except the Swan bands of C<sub>2</sub> which do not differ much in comets and in the laboratory. This matter will be discussed later on.

The (1, 1) band of OH has also been observed in various comets; it extends from  $\lambda 3134$  to  $\lambda 3159$ . Its presence remained in doubt for some time, since the wavelengths of most of the lines coincide with those of low temperature lines of the (0, 0) band of the Fortrat system of CH ( $C^2\Sigma^+ \rightarrow X^2\Pi$ ). However it has now definitely been shown [26] [27], that the faint cometary emissions near  $\lambda 3140$  are due essentially to the (1, 1) band of OH, and that the contribution by CH can only be minor or absent.

The (0, 0) band of NH, transition  $A^3\Pi_i \rightarrow X^3\Sigma^-$ , is usually fairly strong in comets; as in the case of OH, the rotational intensity distribution in comets is, in its essential features, of the low temperature type, but differs in its detailed structure from that of laboratory sources of any kind. The (1, 1) band of NH is not observed. The intensity ratio of the OH and NH bands differs in different comets, and varies also with heliocentric distance [26]. The OH and NH bands of comets were discovered at the McDonald Observatory in 1940 [28].

Progressing toward longer wavelengths we then encounter the (1, 0) band of the violet ( $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ ) system of CN near  $\lambda 3590$  which reveals itself by three fairly broad emissions in most comets. This spectral region contains also the (0, 0) band of  $\text{OH}^+$ , system  ${}^3\Pi_g \rightarrow X^3\Sigma^-$ . There seems to be fair, although not quite conclusive, evidence in favour of the presence of this  $\text{OH}^+$  band in comets [29]; better observational material in this spectral region is desirable. The difficulty of an entirely convincing identification of  $\text{OH}^+$  is due in the first place to the low resolution of the observational material presently available and to blending with the CN band and possibly with other bands (since many molecules have strong emissions in this region). Moreover, the exciting solar spectrum is extremely complex in this region and this, as will be shown later, should lead to a peculiar rotational intensity distribution among the  $\text{OH}^+$  lines [29]. At any rate the (0, 0) band of  $\text{OH}^+$ , which is probably present in comets, is weak, and the transitions corresponding to higher vibrational quantum numbers, such as (0, 1) at  $\lambda 3983$ , (1, 1) at  $\lambda 3695$ , and (1, 0) at  $\lambda 3332$ , must be absent.

The sequences  $\Delta v = 0$  and  $-1$  of the violet system of CN are found in practically all comet spectra. Their rotational profiles which are most remarkable will be discussed in a later section.

On the shortward side of the  $\Delta v = 0$  sequence of CN, occasional weak emissions, confined to the most central region of the coma, have been observed; they are not easily detected on the solar continuum; they have been studied recently, but are still unidentified [30].

On the longward side of the  $\Delta v = 0$  sequence of CN, there appears on strongly exposed spectrograms the  $B^2\Sigma^- \rightarrow X^2\Pi$  system of CH. In comets this electronic transition is much weaker than the  $A^2\Delta \rightarrow X^2\Pi$  system near  $\lambda 4314$ , but stronger than the Fortrat system,  $C^2\Sigma^+ \rightarrow X^2\Pi$ , near  $\lambda 3145$ . The  $B^2\Sigma^- \rightarrow X^2\Pi$  band consists mainly of seven or eight faint emissions, from  $\lambda 3886$  to  $\lambda 3921$  (branches  $Q$  and  $P$ , to  $K = 6$ ), all restricted to the central part of the coma [28]. In the  $A^2\Delta \rightarrow X^2\Pi$  transition the strongest emission is a blend of  $Q$ -lines at  $\lambda 4313$ ; the  $R$  branch which extends on the shortward side contains usually six lines and is stronger than the  $P$  branch observed on the longward side (five lines). The (1, 1) band if present is hopelessly blended in (0, 0). No trace of any line due to carbon deuteride is found. As in the case of OH, NH, and CN, the rotational intensity distributions in the CH system are not the same as in laboratory sources.

Between the strong sequence  $\Delta v = 0$  and the weaker one  $\Delta v = -1$  of CN, almost all comet spectra show a set of emissions centred around  $\lambda 4050$  which we shall call the " $\lambda 4050$  group". We shall discuss this group later on.

In the region  $\lambda 4240$ , three emissions which have been observed in several comets at  $\lambda 4231$ ,  $4238$ , and  $4254$  may be rather convincingly assigned to the (0, 0) band of  $\text{CH}^+$ , transition  ${}^1\Pi \rightarrow {}^1\Sigma^+$  [31]. If this identification is correct three emissions at  $\lambda 3954$ ,  $3963$ , and  $3972$  may be assigned to the (1, 0) band of  $\text{CH}^+$ . All these emissions are  $P$ ,  $Q$ , and  $R$  lines of a low rotational number. These lines are present in the head and in the tail; the extension of  $\text{CH}^+$  into the tail is much shorter than that of  $\text{CO}^+$  and  $\text{N}_2^+$ . The identification of  $\text{CH}^+$  has been discussed by McKELLAR [32], who has tentatively envisaged that certain emissions assigned to  $\text{CH}^+$  might possibly be due to  $\text{SiO}_2$ ; the evidence in favour of  $\text{SiO}_2$  is weak and the identification of  $\text{CH}^+$  may be considered as fairly safely established.

Longward of the  ${}^2\Delta \rightarrow {}^2\Pi$  system of CH lies the strongest emission of the visual region, the Swan system of  $\text{C}_2$ , transition  $A^3\Pi_g \rightarrow X^3\Pi_u$ . Contrary to OH, NH,

CH, and CN which have vibrational and rotational intensity distributions of the low temperature type (although not quite identical with the intensities in low temperature laboratory sources), the Swan system is represented by many vibrational bands, and each band has many rotational lines. In a general way the Swan system is of the high temperature type, roughly similar to a laboratory source at a temperature of the order of  $3000^{\circ}\text{K}$ , although differences in intensity distributions are present. There exist five other well-known systems of  $\text{C}_2$ , one of which, ( $B^3\Pi_g \rightarrow X^3\Pi_u$ ), the Fox-Herzberg bands, is connected to the ground electronic state. The latter is not observable because the only bands longward of  $\lambda 3000$  are too weak. No trace is found of the other systems; their upper electronic states are not connected to  $X^3\Pi_u$  by strong transitions.

Within the Swan system the sequences  $\Delta v = 0$ ,  $+1$ , and  $-1$  are intense; the sequences  $\Delta v = +2$  and  $-2$  are weak. On strongly exposed spectrograms of comets which are not too distant from the Sun, the Swan system is usually richly represented; the sequence  $\Delta v = -2$  may show up to six bands. The relative intensities of the  $\text{C}_2$  bands will be discussed later on.

Several recent papers [33] have emphasized the structure appearing within the Swan bands, and especially between the sequences. Such structures have been described in detail for 1947 XII (bright southern Comet) and for 1948 I (the other bright southern object). While certain details are due to complex intensity distributions within the bands, there is little doubt that a number of fairly weak emissions must be due to as yet unidentified molecular systems.

The visual region of the comet spectra remained rather neglected for a long time. Indeed, observations with sufficient resolving power are still highly desirable. However, a number of interesting results have already been obtained. A few strong emissions appearing only in the central part of the coma (in sharp contrast with the Swan bands extending far into the head), had been observed in the region  $\lambda > 5000$ , especially at  $\lambda 5978$  (int. 4),  $5996$  (2),  $6299$  (6),  $6334$  ( $2^+$ ),  $6621$  ( $2^+$ ). It was shown in 1943 [34] that these emissions belong to the  $\alpha$ -band of ammonia, assigned to the  $\text{NH}_2$  radical. Many other weaker emissions in the region  $\lambda > 5000$  seemed to belong to the same  $\text{NH}_2$  molecule [34] [35]; PROSY [36] added a number of suggested identifications in the region  $\lambda 4250$  to  $\lambda 6440$  on the basis of his laboratory investigation of discharges in ammonia vapour. The analysis of the  $\text{NH}_2$  spectrum which is at present in progress [37] should contribute considerably to clearing up the visual region of comet spectra.

When a comet approaches the Sun to about  $0.8 \text{ A.U.}$ , the sodium  $D$ -doublet appears [38]; this yellow line may actually reach a very high intensity at small heliocentric distances. The brightness of Comet 1882 II (WELLS) near perihelion was due almost entirely to the Na-emission; the same is true for Comet 1927 IX (SKJELLERUP).

Two problems which remain rather unsettled concern the red ( $A^2\Pi \rightarrow X^2\Sigma^+$ ) system of CN, and the as yet hypothetical intercombination transition  $B^2\Sigma^+ \rightarrow A^2\Pi$  of CN. Attention was focussed on the red system of CN, despite the low transition probabilities of the red CN bands below  $\lambda 9000$  compared with the (0, 0) violet band, as a result of the observation in 1947 XII of strong emissions at  $\lambda 7906$  and  $\lambda 8106$ . It was the first time that the infra-red photographic region of a cometary spectrum had been covered [39], and only two strong emissions appeared between  $\lambda 6700$  and  $\lambda 8900$  ( $\lambda 8900$  was the limit of the ammonia-hypersensitized IN-emulsion). The emissions  $\lambda 7906$  and  $\lambda 8106$  are strong (of the same order as the (0, 0) violet band of

CN), but are confined to the central part of the coma, instead of extending far out into the head, as the CN or  $C_2$  bands do.  $\lambda 7906$  is stronger than  $\lambda 8106$  by a factor of 2 or 3. The identification of these two infra-red emissions is fraught with difficulty, especially on account of the low resolution used. The almost perfect coincidence with a vibration-rotation band of ammonia observed in the major planets led to an attempt to assign the new emission to a polyatomic molecule. Beside  $NH_3$ , other polyatomic compounds—hydrogen cyanide HCN, acetylene  $C_2H_2$ , carbon dioxide  $CO_2$ —have bands at or near  $\lambda 7906$  and  $\lambda 8106$ , although the intensity profiles of these bands drawn by HUNAERTS [40] do not agree perfectly with the cometary profiles. However, there is a general objection to the assignment of a cometary emission to any vibration-rotation band appearing in this region. Such bands have always a small absorption intensity; hence it would be surprising to find them in emission when there are much stronger absorption bands in the ultra-violet that would lead to photodissociation. Finally, it was found preferable to consider the diatomic molecules as possible emitters of  $\lambda 7906$  and  $\lambda 8106$ .

A fairly good coincidence in wavelength arises with the (2, 0) and (3, 1) bands of the red system of CN; the CN profiles are also reasonably similar to those of the cometary emission [41]. It seems at present plausible to assume that the (2, 0) and (3, 1) red bands are really responsible for the cometary bands. However, two serious difficulties remain: (1) the  $f$ -value of the (2, 0) red band of CN is small compared to the (0, 0) violet band [39], while the infra-red cometary emission is about as strong as  $\lambda 3880$ ; (2) the infra-red emissions are confined to the central part of the coma, while the violet bands extend far out into the head. It would thus seem that the red and violet systems cannot be excited by the same mechanism. Some mechanism other than fluorescence—well established for the violet system—should be found for the infra-red emissions. Since the  $A^2\Pi$  state of CN has a low energy it was first thought that the solution may be found in a process of photodissociation of a parent-molecule, but grave difficulties are encountered. The infra-red bands may possibly be excited by the collision of solar particles.

If we assume the assignment of  $\lambda 7906$  and  $\lambda 8106$  to red CN bands to be correct, we should examine the possibility that other red CN bands corresponding to higher vibrational transitions may also be present. Indeed eight or nine emissions between  $\lambda 5730$  and  $\lambda 6641$  agree reasonably well with bands of the sequences  $\Delta v = 5$  and 4 of the red system [34] [26] [28] [42]. Actually the (4, 2), (3, 0), and (4, 1) bands appear also to be present in the near infra-red region [26].

Since the violet  $B^2\Sigma^+ \rightarrow X^2\Sigma^+$  system of CN is strong in comets, and since the red  $A^2\Pi \rightarrow X^2\Sigma^+$  system appears to be also present (and possibly strong), one may wonder whether the intercombination system  $B^2\Sigma^+ \rightarrow A^2\Pi$  could not be observed. As far as we know, this transition has never been found in the laboratory; however, since the corresponding system has been observed for  $CO^+$  (Baldet-Johnson bands), the search for it should have some meaning. "Synthetic profiles" have been prepared for many bands of the intercombination system by J. HUNAERTS [43], and their theoretical relative transition probabilities have been estimated. Limiting ourselves to the (0, 0), (1, 0), and (0, 1) bands, maxima should appear near the following wavelengths:

(0, 0)	6002	(1, 0)	5323	(0, 1)	6724
	5989		5313		6708
	5981		5307		6698



The available observational data do not exclude this identification; however, a still unfinished discussion is required before anything more may be stated.

### 3. DESCRIPTION OF THE SPECTRUM OF THE TAIL

For many years the main characteristics of the tail spectrum\* have been known to be the "comet-tail system"  $A^2\Pi_i \rightarrow X^2\Sigma^+$  of  $\text{CO}^+$  and the "negative system"  $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$  of  $\text{N}_2^+$ , the lower electronic levels of these systems being the ground states of  $\text{CO}^+$  and  $\text{N}_2^+$ . As was mentioned before  $\text{CH}^+$  emission is also observed in the tail in the neighbourhood of the head. Tails have been observed in which the solar continuum or the CN bands were strong. Comet 1947 k (BESTER) provided a good opportunity for securing for the first time slit spectrograms of fair resolution extending into the ultra-violet to  $\lambda 3370$ .†

In addition to the known bands the slit spectrograms of the tail of Comet 1947 k (BESTER) revealed many emissions, most of which were rather weak, although three at  $\lambda 3378$ , 3509, and 3674 reach a considerable intensity [26]. The  $(v', 0)$  and  $(v', 1)$  progressions of the comet-tail system of  $\text{CO}^+$  are observed from  $v' = 6$  to  $v' = 1$  [44]. The profiles and longward shifts of these bands [26] [42], are consistent with a rotational temperature of the order of  $300^\circ\text{K}$ ; the intensities within a vibrational progression differ from those in the laboratory, which is quite understandable. In the astronomical region the  $\text{CO}^+$  molecule possesses another transition, the "Baldet-Johnson System", connecting the upper level  $B^2\Sigma^+$  of the first negative system with the upper level  $A^2\Pi_i$  of the comet-tail system. WURM [45] has suggested that this  $B^2\Sigma \rightarrow A^2\Pi$  transition should be found in comet tails. Indeed, the  $(0, 0)$ ,  $(0, 1)$ ,  $(1, 0)$ , and  $(2, 0)$  transitions of the Baldet-Johnson system have been found in the tail spectra of Comet Bester [26]. The levels  $v' = 0, 1, 2$  of the Baldet-Johnson system are reached from the ground state  $X^2\Sigma^+$  ( $v'' = 0$ ) by means of the  $(v', 0)$  bands of the first negative system  $B^2\Sigma^+ \rightarrow X^2\Sigma^+$  at  $\lambda 2189.8$ , 2112.4, and 2042.3. The solar radiation in this region is much weaker than in the violet region; this fact, added to the lower  $f$ -values usually assumed for the B.J. relative to the C.T. system, accounts for the observed weakness of the B.J. system compared with the C.T. transition.

The  $(0, 0)$  band of  $\text{N}_2^+$  is strong; its width indicates a "rotational temperature" higher than that for  $\text{CO}^+$ . Most other  $\text{N}_2^+$  transitions are blended.

After the  $\text{CO}^+$  and  $\text{N}_2^+$  bands have been identified, there remain a number of unassigned tail emissions, three of which, at  $\lambda 3378$ , 3505, and 3674, are outstanding. These wavelengths agree closely with those of the origins of the  $(1, 0)$ ,  $(0, 0)$ , and  $(0, 1)$  transitions in the  $^2\Pi_u \rightarrow ^2\Pi_g$  spectrum of  $\text{CO}_2^+$ , recently analysed by MROZOWSKI [46].  $^2\Pi_g$  is the ground electronic state of  $\text{CO}_2^+$ ; the bands have a fairly simple structure, the  $\text{CO}_2^+$  molecule being linear in both  $^2\Pi$  states. All the strong bands observed in the laboratory may be attributed to symmetrical vibrations,  $\nu_1$ , the  $\text{CO}_2^+$  molecules remaining in their lowest states of  $\nu_2$  (bending), and  $\nu_3$  (anti-symmetrical vibrations). The  $\text{CO}_2^+$  identification in comets is convincing; recent work on the theoretically expected profiles of the bands [42] confirms the assignment;

\* It should be noted that while the  $\text{CO}^+$  emission is especially prominent in tails, it is also present in the central part of the coma, even toward the Sun. However, the extension toward the Sun is rather small.

† As far as we know the only slit spectrograms of comet tails which had been taken prior to 1940 were those of Comet 1908 III (MOREHOUSE), by CAMPBELL and ALBRECHT (*Lick Bull.*, 1908, 5, 58) and by H. D. CURTIS (*ibid.*, 1909, 5, 135) and those of Comet 1911 V (BROOKS) by WRIGHT (*ibid.*, 1912, 7, 8). They extended from  $\lambda 3850$  to  $\lambda 4800$ . The ultra-violet spectrum of the tail of Comet 1907 IV (DANIEL) had been observed by J. EVERSHED with a slitless spectrograph to  $\lambda 3580$  (*M.N.*, 1907, 68, 16). Ultra-violet spectra of the tail of Comets 1908 III (MOREHOUSE) and 1911 V (BROOKS) were also observed with slitless spectrographs by DE LA BAUME PLUVINEL and BALDET, the first to  $\lambda 3269$ , the latter to  $\lambda 3790$  (*Comptes Rendus*, 1912, 154, 1286; 1908, 147, 606; 1909, 148, 759; *Ap. J.*, 1911, 34, 89). SLIPPER and LAMPLAND (*Lowell Bull.*, 1911, 2, 8) observed the spectrum of the tail of Comet 1910 II (HALLBY) to  $\lambda 3585$ .

eight tail emissions turn out to be due to  $\text{CO}_2^+$ . This molecule may thus be added to the three previously known tail molecules:  $\text{CO}^+$  (strong bands),  $\text{N}_2^+$  (strong (0, 0) band), and  $\text{CH}^+$  (weak emission); the presence of  $\text{OH}^+$  remains still somewhat in doubt. The  $\text{CO}_2^+$  ion extends into the tail to shorter distances from the head than  $\text{CO}^+$  or  $\text{N}_2^+$ . It is well known that  $\text{CO}_2$  dissociates into  $\text{CO} + \text{O}$  by absorption of radiation near  $\lambda 1700$  [47]. The identification of  $\text{CO}_2$  indicates that by absorption of ultra-violet solar radiation an appreciable portion of  $\text{CO}_2$  becomes ionized.

The  $\text{CO}_2^+$  emissions also appear strongly in Comet 1941 I (CUNNINGHAM) [48]; they had not been observed with certainty in comet tails before, probably because no ultra-violet slit spectrogram of tails had been obtained prior to 1940. There still remain a few weak unassigned ultra-violet and violet emissions in the tail spectra. Moreover, we have practically no observation of the red region of tail spectra. The presence of NO bands ( $\beta$  system,  $B^2\Pi \rightarrow X^2\Pi$ , 0-9 transition,  $\lambda 3376$ - $\lambda 3386$ ) is not excluded, although it is hard to understand how NO molecules could live for hours or days in the tail without becoming photo-dissociated or photo-ionized.

#### 4. THE EXCITATION MECHANISM

On various occasions we have stressed the fact that the intensity distribution within the cometary bands differs from those found in laboratory sources even at low temperatures. Until 1941 numerous fruitless attempts had been made to interpret these peculiar distributions [28] [49]. The CN band near  $\lambda 3880$  provides a striking illustration. Instead of showing smooth rotational intensity distributions within the *P*-branch (forming the head on the longward side) and the shortward degraded *R*-branch, cometary spectra reveal complex CN profiles. Even with moderately low dispersions the *P* branch presents at least two maxima, one near *P*(3) and one near the head, with a deep minimum around *P*(5); similarly the *R* branch has a maximum near *R*(1) and a deep minimum around *R*(3). Different comets differ in the profile of CN bands. At times it was thought that the comet head contained two or more kinds of CN radicals, resulting from the photo-dissociation of different parent molecules [49] and having different rotational temperatures [28]. It was also suggested that the selectivity was similar to that observed by HERZBERG in the laboratory in exciting the CN bands in active nitrogen. With higher resolution the structure appears even more complex. If the rotational structure is resolved [32] [50], the individual CN lines follow each other with most irregular intensities. Similar, although less striking, results are observed for CH, OH, and  $\text{CH}^+$ , as well as for the other bands of the violet system of CN.

The general interpretation of these complex profiles was given in 1942 [51]. It has usually been assumed in recent years that the main molecular bands, and also the Na lines, are emitted in a fluorescence process excited by solar radiation. As we have seen in the case of the red bands of CN, there seems to be a need for an additional mechanism: whether the latter is the photo-dissociation of a parent molecule, or whether the old "cathodic hypothesis" defended long ago by DESLANDRES should be revived and modernized, will be examined later. The suggestion that cometary emission results from fluorescence was actually put forward by K. SCHWARZSCHILD and KRON in 1911 [52], and developed theoretically by ZANSTRA in 1928 [53] and by WURM in 1934 [54]. The main result of ZANSTRA and WURM is that the observed luminosities of comets having strong emission spectra are of the order of those calculated on the basis of a fluorescence excitation. All the cometary phenomena

indicate also that collisional effects must be unimportant in cometary atmospheres.

An observational test of the fluorescence hypothesis was provided by ÖHMAN's measurements of polarization which do indicate that fluorescence is operative in comets.

Let us assume that the excitation of the CN cometary molecules is due exclusively to the absorption of solar radiation. The population in an excited rotational level  $K'$ , from which the two emission lines  $P(K' + 1)$  and  $R(K' - 1)$  arise, can then be expressed as follows\*:

$$N'_{K'} \propto N''_{K'+1} \cdot p_P^{\text{abs.}} \cdot I_P + N''_{K'-1} \cdot p_R^{\text{abs.}} \cdot I_R, \quad \dots (1)$$

where  $N''_{K'-1}$  and  $N''_{K'+1}$  are the populations in the rotational levels  $K'' = K' - 1$  and  $K'' = K' + 1$  of the ground electronic and vibrational state;  $p_P^{\text{abs.}}$  and  $p_R^{\text{abs.}}$  the transition probabilities of the absorption lines  $P(K' + 1)$  and  $R(K' - 1)$ ; and  $I_P$  and  $I_R$  the intensities of solar radiation for the wavelengths of  $P(K' + 1)$  and  $R(K' - 1)$ , corrected for the radial velocity of the Sun with respect to the comet (ordinarily this correction is of the order of  $\pm 0.25 \text{ \AA}$ ).

Whatever the distribution  $N''_{K''}$  may be,  $N'_{K'}$  will depend on the profile of the solar radiation. If one plots the wavelengths of  $P$  and  $R$  lines on the Utrecht Photometric Atlas of the Solar Spectrum, it appears strikingly that the deep minima in the solar spectrum in the region of  $P(6)$  and  $P(7)$  and between  $R(2)$  and  $R(7)$ , due to strong Fraunhofer lines, are undoubtedly the cause of the very low intensity of the  $P$  and  $R$  lines corresponding to  $3 < K' < 8$ . Whatever the radial velocity of the comet relative to the Sun may be,  $P(6)$  and  $P(7)$  will always fall in a deep minimum of the solar spectrum, caused mainly by  $\lambda 3878.02$  (Fe I, solar int. 8) and  $\lambda 3878.57$  (Fe I, solar int. 7). By examining carefully the solar absorption lines it is possible to explain qualitatively in a convincing manner the observed structures in cometary bands. The radial velocity may have an important effect in bringing a specific cometary absorption line inside or outside a strong Fraunhofer line. It was known that comets observed at the same heliocentric distance sometimes showed different CN-profiles; these differences are fully explained by radial velocity effects. It is obvious that similar considerations may be applied to the other molecules: OH, NH, CH,  $C_2$ , . . . .

The first more or less quantitative tests of this hypothesis were made by McKELLAR [55] for the CN and CH bands of Comets 1939 III (JURLOF), 1941 I (CUNNINGHAM), and 1943 I (WHIPPLE). McKELLAR adopted a Boltzmann-type of distribution for the rotational levels of CN in the ground state. The "rotational CN temperatures" were chosen to give the best agreement in wavelength between the observed main maximum of the  $P$  branch of the (0, 0) band of CN and the corresponding maximum of the computed intensity curve. In applying formula (1) the intensities were taken from the Utrecht Photometric Atlas of the Solar Spectrum with due correction for radial velocity shift. The computed relative intensities of the emission lines were then plotted as rectangles of a height proportional to the calculated intensity and a width equal to the projected spectrographic slit width [60]. A few obvious transformations of the calculated diagrams were applied in order to make them as nearly comparable as possible with actual profiles. Every observed apparent maximum has its corresponding counterpart in the calculated profiles. Had the effect of the contour of the

\* This assumes that the molecules in the ground electronic level are all in the lowest vibrational state. In general there should be a summation over the different  $v''$ -levels, account being taken of the different absorption probabilities.

solar spectrum been neglected, the calculated profiles would have been smooth with no subordinate maxima.

These results provided the most direct observational proof of the fluorescence mechanism of cometary emission.

The radial velocity of the comet relative to the Sun affects considerably the rotational profiles. This effect has been found for CN, OH, NH, and CH. It may even influence appreciably the total intensity of a cometary band. The heliocentric distance  $r$  also affects the profiles: there is an increase in "rotational temperature" of the CN molecules as  $r$  decreases. This effect had been found previously [57] [28], but became more clearly defined [55]. The "rotational temperatures" found for CN are of the order of 300 or 400°K, depending on  $r$ .

When the rotational structure of CN had been totally or partially resolved [32] [50], the observed intensities of the individual CN lines agree with the theoretically expected values.

Qualitatively the resonance mechanism explains readily the profiles of the CN, CH, OH, NH, and CH<sup>+</sup> bands. Quantitative discussions beside those of MCKELLAR have been performed by J. HUNAERTS [27] [40] [42], J. DUFAY, FEHRENBACH, and COURTES and others. At first a Boltzmann distribution among the rotational levels of the ground electronic state was assumed. Actually such an assumption is not justified, since the conditions for thermodynamic equilibrium are not fulfilled (no collisions!). A first logical extension consists in obtaining from the observed intensity profile of a given molecular band the distribution of molecules among the rotational levels of the excited electronic state involved in its production; from this, assuming the resonance mechanism, one may derive the relative populations on the rotational levels of the ground electronic state. Such work was done by MCKELLAR [58] for the CH molecule, using the 24315 band as observed in the spectrum of Comet 1941 I at  $r = 0.54$  A.U. MCKELLAR found that nearly all the CH molecules exist in the two lowest rotational levels,  $K'' = 1$  and  $K'' = 2$ , of the normal  $^2\Pi$  state. POLOSKOV [59] has also contributed to this problem.

In the absence of collisional effects, the primary mechanism which is involved in populating the vibrational and rotational levels of the ground electronic state is the absorption of solar radiation. This point was stressed by WURM [60] and may easily be illustrated in the case of the (0, 0) violet band of CN which has no  $Q$ -branch. In absorption, the  $R(K)$  line is stronger than  $P(K)$ ; this tends to overpopulate the level  $K' = K + 1$  relative to  $K' = K - 1$  in the excited electronic state. In the emission from  $K' = K + 1$ , the  $P(K + 2)$  line is stronger than  $R(K)$ : this tends to populate the higher  $K''$  levels. If the solar radiation did not have absorption lines, we should expect a smooth distribution among the rotational levels. Whether this distribution would be of the low- or of the high-temperature type depends on the depopulating process. Downward transitions between rotational levels belong to the pure rotational far infra-red spectrum. If this spectrum is theoretically permitted—which is the case for heteronuclear diatomic molecules—the downward transitions will be able to depopulate the  $K''$  levels. The deciding factors are evidently the relative values of the time between successive absorption processes and the lifetime of the rotational states. We may thus understand why the bands of CH, OH, NH, CN, and CH<sup>+</sup> have, on the whole, low temperature rotational distributions. Of course, beside the heliocentric distance, the individual characteristics of the molecules are also of utmost importance in determining the actual distributions. These characteristics are mainly

the dipole moments and the band structure (*e.g.*, the presence of a strong  $Q$  branch, as in CH, reduces the tendency of molecules to reach higher  $K$  values).

The situation is quite different for a homonuclear molecule such as  $C^{12}C^{12}$ , for which the pure rotational spectrum is forbidden. Molecules may then accumulate on higher rotational levels and simulate a high-temperature rotational distribution. Considerations of a similar character apply to the vibrational levels.

It is easily seen that, as a result of the influence of the solar absorption lines, a more or less irregular distribution amongst the rotational states  $K''$  may be brought about. This explains McKellar's result in the case of the CH molecules.

These considerations illustrate the artificial character of the concepts of vibrational and rotational "temperatures" of cometary bands. The "temperatures" obtained from different molecules may differ considerably. At the same heliocentric distance the rotational temperature which best fits a CN profile may be  $435^\circ\text{K}$ , while the CH profile would require  $200^\circ\text{K}$ .

The profiles of the  $C_2$  bands in comets have been studied by J. HUNAERTS [61] and by Ch. FEHRENBACH and G. COURTÈS [62]; the most recent investigation is that by A. MCKELLAR and J. L. CLIMENHAGA [63]. For  $C_2$  the rotational and vibrational temperatures obtained for the ground electronic level agree rather well; they are of the order of  $3000$ – $4000^\circ\text{K}$ . A variation of heliocentric distance affects the "temperature" of  $C_2$  bands, just as it does for CN. The synthetic profiles of the  $C_2$  bands interpret certain anomalous emissions observed between the  $C_2$  heads which are actually due to the distortion of the profiles caused by the solar absorption lines. However, this does not explain all the emissions which have been observed within the Swan sequences.

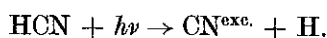
Assuming that the resonance mechanism is totally responsible for the cometary emission of bands such as OH, CN, . . . , it is possible to obtain valuable data on the lifetimes of molecules in rotational levels, by following the theory of cyclical transitions [64]. A remarkable application of this idea has been made by J. HUNAERTS [27] to the case of OH, for which the absolute transition probabilities in the  $(0, 0)$  band are known [65], as well as the relative transition probabilities of the different vibrational bands [66]. HUNAERTS showed that it is impossible to interpret correctly the OH-comet band if a Boltzmann rotational distribution on the lower electronic level is assumed. Starting from molecules which are all on the rotational level  $K'' = 0$  of  $^2\Pi_{1/2}$  and  $^2\Pi_{3/2}$  ( $J'' = 1/2$  and  $3/2$ ) the observational data are satisfactorily interpreted if a single absorption and re-emission process is admitted. In other words infra-red transitions between the lowest  $K''$ -levels must take place more frequently than the successive absorptions of solar radiation (average time interval at  $r = 1$  A.U. of the order of 500 sec.). The transition probability for the pure rotational line of OH is thus greater than  $2 \times 10^{-3} \text{ sec.}^{-1}$ .

The other cometary molecules may be treated in a similar way, once the corresponding absolute  $f$ -values are known. It seems probable that all hydrides will give similar results. In the case of  $C_2$  which has no permanent dipole a temperature of the order of  $3000^\circ\text{K}$  for the ground electronic state accounts for the comet spectra. A Boltzmann rotational distribution in the upper electronic state corresponding to  $T = 5000$  to  $7000^\circ\text{K}$  gives similar results, although not quite so satisfactory. The case of CN is intermediate between the hydrides and  $C_2$  as far as the number of populated rotational states is concerned; however, the CN bands correspond to a low temperature like the hydride bands. At any rate the lifetime of the lower  $K''$

rotational levels of CN is greater than the average time between two absorption processes [27].

These considerations show that identification should proceed with great caution, since the intensities in comets may differ so much from those in the laboratory. Wavelength coincidences are only a first indication. The final test of an identification should be based on the subdivision of the exciting radiation into a number of monochromatic excitations. The excited pattern is the superposition of resonance doublets (or singlets or triplets according to the type of electronic transition), each consisting of a *P*- and an *R*-line, and each having a specific intensity. We should thus not expect the pattern to resemble closely the intensity distribution in a laboratory spectrum, even in a low temperature source [67]. "Synthetic profiles" are of the greatest help.

While there is no doubt that the CN (violet), OH, NH, and CH bands are emitted by fluorescence, there remains the possibility that other bands may be excited by some other mechanism. This could be the case especially if the excited level of the band has a low energy. A band may be excited in a process of photo-dissociation of a parent molecule, of the kind



Or it may be excited by collision of a solar electron or proton or other particle; this latter process will be considered again later.

If fluorescence is completely or partially absent for a band, it would be observable in the profile of the band and in its polarization.

When examining a possible identification, attention should also be given to the physical properties of the molecule. Let us take as an example the case of the  $\text{O}_2$  molecule. When the first ultra-violet slit spectrograms of comet tails were obtained in 1948, a few intense emissions remained unassigned. They coincided strangely with several bands of the Schumann-Runge ( $B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ ) system of  $\text{O}_2$ . Yet despite the striking coincidences the assignment of the ultra-violet emissions to  $\text{O}_2$  was rejected for the following reasons: (a) the relative position of the potential energy-curves of  $\text{O}_2$  is such that the excitation of  $\text{O}_2$  from the ground state  $X^3\Sigma$  to the excited level  $B^3\Sigma$  will frequently lead to dissociation; (b) the relative intensities among the vibrational bands arising from the same excited level  $v' = 0$  were abnormal and could not be explained.\*

Later on these unexplained tail emissions turned out to be due to  $\text{CO}_2^+$ .

Numerous examples of critical discussions of identifications have been published recently [26] [39] [40] [42].

Seventy years ago two excellent observers, LOHSE and COPELAND, announced [68] that they had observed emission lines of iron and nickel in the bright Comet 1882 II which came very close to the Sun (perihelion distance 0.008 A.U.). This announcement has usually encountered scepticism since the relative intensities of the Fe- and Ni-lines given by LOHSE and COPELAND differ strongly from the laboratory values. However, this scepticism is actually not founded. The Fe- and Ni-atoms would be at a fairly low "temperature", lower than 1000°K and would absorb only from fairly low electronic levels. Moreover, the exciting solar radiation contains many

\* It seems impossible in the case of an  $\text{O}_2$ -molecule to find a mechanism which would provide the velocity required for an extended tail length. Radiation pressure on  $\text{O}_2$  is expected to be weak, since the bands starting from  $v' = 0$  are in the region of  $\lambda 1800$ , where the solar radiation is already fairly weak. As for BREMMANN's mechanism (acceleration by solar ionized particles) it applies only to ions.

Fe, Ni, and other absorption lines. It may very well be that lines which are weak in the laboratory are actually strengthened in the comet relative to stronger lines; also that the solar lines create unusual intensity ratios even within multiplets. From a rough examination the announcement of COPELAND and LOHSE appears quite plausible [69]; a more thorough discussion may be interesting.

In the course of the description of the comet spectrum certain as yet unassigned or doubtfully assigned emissions have been mentioned. These are: weak features shortward of the (0, 0) violet band of CN; the  $\lambda 4050$  group; sharp lines in Comet Encke [70]; emissions between and within the Swan sequences; weak lines in the visual region; a few features in the tail spectrum; possibly  $\lambda 7906$  and  $\lambda 8106$ . For some of these features it would definitely be better to postpone new attempts at identification until better observational data are available about their wavelengths, behaviour with heliocentric distance and distribution in the head or tail [71]. However for the most striking unidentified emission, the " $\lambda 4050$  group", our observational data are already fairly good: we have excellent wavelengths, and the band has been observed in many comets at many heliocentric distances.

### 5. THE " $\lambda 4050$ GROUP"

The strong cometary emission lines concentrated in the central region of the coma and covering the range  $\lambda 3950$  to  $\lambda 4150$  have been the subject of scores of publications. The observations and tentative assignments prior to 1940 were discussed by BOBROVNIKOFF [72] and by SWINGS, ELVEY, and BABCOCK [28]. The intensity of 4050 relative to all other emissions—except possibly the  $\text{NH}_2$  emission of the red region, the behaviour of which relative to 4050 has never been well investigated—increases with heliocentric distance; at  $r = 2.2$  A.U. the 4050 emission remains strong while the CH and  $\text{C}_2$  lines have disappeared. On low dispersion spectrograms the 4050 lines appear sharp, like atomic lines or individual rotational lines. However, recent observations by JOSE and SWINGS [33] with somewhat higher resolution show that the emissions are definitely wider than the individual rotational lines of the CH-band. The 4050 emissions are not quite as concentrated near the nucleus as are the CH-lines; their intensity distribution within the head may differ appreciably from that of CH. None of these lines has ever been found in interstellar absorption.

Up to 1942 the 4050 group was attributed tentatively to all kinds of spectra of diatomic molecules: a new system of  $\text{C}_2$ , tail bands of CN, bands of CH, of NaH, etc. . . . In 1942 the suggestion was made by HERZBERG [73] and the author [74] that the  $\lambda 4050$  emission may be due to a polyatomic molecule consisting of elements of high cosmic abundance (H, C, N, O). At that time the  $\text{CH}_2$  molecule appeared especially promising [75]: HERZBERG [73] showed that the 4050 group may be a  $\perp$  band of a nearly symmetric top molecule. Some time later HERZBERG [76] was able to produce a laboratory spectrum which appeared very similar to the cometary emission; the band was obtained in an interrupted discharge through streaming methane. The conditions of excitation in the laboratory supported the assumption that the group is due to  $\text{CH}_2$ . However, the assignment to  $\text{CH}_2$  by HERZBERG was only a tentative one, and the possibility of an other assignment was left open.

Generally, however, this identification was accepted, and it was thought that the  $\text{CH}_2$  molecules in comets result from the photo-dissociation of methane. Moreover it was often stated that the CH radicals result probably from the photo-dissociation of  $\text{CH}_2$ ; this is, however, not fully supported by the cometary observations.

A considerable amount of experimental work has been devoted to the 4050 laboratory spectrum in recent years [77]. The main results are that the molecule does *not* contain hydrogen and that it has at least two carbon atoms. As seems to be indicated by experiments made by DOUGLAS in which an isotopic mixture of  $C^{12}$  and  $C^{13}$  was used (roughly in equal amounts), a  $C_2$ -molecule appears to be a good guess.

Actually a comparison of astronomical and experimental data as they existed in 1950 had already led to the same tentative suggestion. It was based essentially on the fact that, most probably, the absorption structure observed in the violet region of late N-stars [78] is due to the same molecule as that responsible for the 4050 emission in comets. Assuming the identity of the molecule in comets and in N-stars, one may conclude that the molecule is a neutral polyatomic molecule, containing no oxygen. From the work of MONFILS and ROSEN it was known that the molecule contains no hydrogen. Thus the molecule must be of the  $C_xN_y$  type. Astronomical and laboratory observations indicated that nitrogen is not involved. Moreover, from theoretical considerations a triatomic molecule appeared more likely than a bigger one to be abundant in a carbon-star. Hence  $C_3$  was tentatively suggested in 1950 [79].

While all the recent laboratory investigations confer a high probability to the  $C_3$  assignment further experimental work is required. Moreover, since the structure of the emission is simpler in comet spectra than in most laboratory sources, one may try to find a vibrational classification of the bands on the basis of the comet data. Indeed, it is possible [80] to group the main cometary emissions into three progressions corresponding to transitions to  $v' = 0, 1, 2, 3, 4$  from the three vibrational levels  $(0, 0, 0)$ ,  $(1, 1, 0)$ , and  $(2, 2, 0)$ .

The relation of this problem to recent spectroscopic investigations on phenomena in flames, pyrolysis, and photolysis [81] is extremely interesting. The 4050 group has now been observed in emission or in absorption in certain flames, in explosions caused by photoflash, and in various other sources. Such work provides important clues with regard to the identification of the "4050 molecule".

It is interesting to note that in various laboratory sources giving rise to 4050, hydrogen is required, although the 4050 molecule does not contain hydrogen. In the hollow cathode 4050-molecules are formed by impact of H on the graphite walls.

Could the 4050-molecules in comets not be formed by the impact of solar protons on the solid nuclei, or on the sublimated molecules containing carbon immediately surrounding the nuclei? One may easily show that the abundance of 4050-molecules obtained in this fashion may possibly be compatible with the observations. Such a mechanism would explain why the 4050-molecules behave differently from all other molecules, in relation to heliocentric distance.

Of course, in such a case we should expect the "4050 activity" to be related to solar activity and to the sudden brightening up of comets. One may even wonder whether the emission itself does not result from the collision process. It would be possible to check on the absence of fluorescence excitation by measurement of the polarization in the 4050 group, and by study of the profile (once the 4050 spectrum is classified). Should it turn out that the 4050 group is really emitted by collision, one would feel greatly tempted to consider a similar type of excitation to explain the red system of CN. The behaviour of the intensity ratio of 4050 and 7906 would indeed be profitably investigated.



## 6. PHYSICAL CONSIDERATIONS

The future identifications should be conducted with all the spectroscopic precautions which have been mentioned previously, also taking into account the behaviour with heliocentric distance and the distribution within the head or tail.

It is possible to find numerous wavelength coincidences between cometary emissions and bands due to various molecules, including FeO, and also, although less strikingly, NiO, CrO, and CaO (B. ROSEN and P. SWINGS, unpublished). For example, the FeO bands, 4448, 4544, 4604, 5790, 5807, 5903, 6097, 6110, 6219, *etc.*, are close to cometary emissions. However, such coincidences appear to be purely accidental.

There are good hopes that recent experimental work will lead to new identifications. The laboratory spectra of organic substances recently obtained by SCHÜLER [82] appear especially promising. The investigated molecules are all fairly simple compounds of H, C, N, and O, of the type which may be envisaged as parent molecules for the OH, NH, CH, CN, NH<sub>2</sub>, *etc.*, radicals (see later). One of SCHÜLER's spectra due to C<sub>2</sub>H<sub>2</sub> appears especially interesting. Actually all the spectroscopic investigations of discharges in gases which may be expected in comets are of great interest; typical of such useful work is that by G. HERZBERG, J. KAPLAN, R. and L. HERMAN, and P. PROISY.

Careful attention must also be given to the spectroscopic investigations of phenomena in flames, explosions, pyrolysis, and photolysis, since most molecules which are thus encountered are rather simple compounds of H, C, N, and O; such investigations have already been mentioned with respect to the 24050 group. They will, of course, be useful also for the other unassigned radiations. As an example, a spectrum obtained by GAYDON and WOLFARD [83] in some flames, such as those of acetaldehyde, ether, and acetone, should be mentioned: it has an open rotational structure, characteristic of a hydride; it is located in the region 25300 to 26400, where numerous weak unassigned emissions concentrated in the central part of the coma are located. Many recent investigations by GAYDON, WOLFARD, PARKER, NORRISH, PORTER, EMELEUS, and others should be examined with the comet problem in mind. Obviously the excitation conditions in flames and in comets are extremely different, and the appearances of the bands should thus differ in these two sources.

As has been demonstrated in the case of the 24050 group, a comparison between the spectra of comets and those of cool stars is sometimes useful. Further comparisons involving the visual region would probably be fruitful also. It seems likely that cool stars will be found in which the NH<sub>2</sub>-band is present.

Actually a great deal of experimental spectroscopic data are still lacking, for diatomic as well as polyatomic molecules. It appears probable that the spectra of ions, such as CN<sup>+</sup> or C<sub>2</sub><sup>+</sup>, which are still unknown play a rôle in comets; the investigation of NH<sup>+</sup> should be continued [84]. Nothing is known about doubly ionized molecules such as CH<sup>++</sup>, CO<sup>++</sup>, CO<sub>2</sub><sup>++</sup>. As for polyatomic molecules, we still need the analysis of electronic spectra of simple molecules like NH<sub>2</sub>, SiO<sub>2</sub>, NO<sub>2</sub>, *etc.*, and we know nothing (or almost nothing!) about CH<sub>2</sub> [75], C<sub>2</sub>H, CH<sub>3</sub>, *etc.*

For the studies of profiles and of abundances, and for other photometric investigations, we still need experimental and theoretical work on the transition probabilities of most molecular bands. A good start has been made for OH [65] [66] and for C<sub>2</sub> [85]; but little is known with respect to the other molecules. The *f*-value of the OH-band is much smaller than that of CN or CH; despite the faintness of the

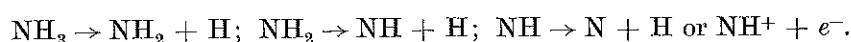
OH-bands, the abundance of the OH-radicals must be comparable to that of CN, or even larger.

The sequence  $\Delta v = +1$  of the Swan system sometimes reveals the bands of the isotopic  $C^{12}C^{13}$  molecule (and possibly of  $C^{13}C^{13}$ ) [86], in a way more or less similar to the carbon-stars. However, as far as we know, no comet presenting the high abundance ratio  $C^{13} : C^{12}$  (about 3 : 1) found in many carbon stars has ever been observed. The most characteristic  $C^{12}C^{13}$  band is (1, 0) at  $\lambda 4745$ , which falls in a clear region of the comet spectrum. The (2, 1), (3, 2), and (2, 0) bands of  $C^{12}C^{13}$  seem also to have been occasionally present. An emission has sometimes been observed at the position of the (1, 0) band of  $C^{13}C^{13}$ ,  $\lambda 4753$ . However, this assignment to  $C^{13}C^{13}$  is plausible only when  $\lambda 4745$  is present and much stronger, since there seems to be an additional unidentified radiation near  $\lambda 4753$ . Assignments of cometary emissions to  $C^{13}C^{13}$  indeed remain doubtful. Although no photometric measurement of the relative intensities of the  $C^{12}C^{12}$  and  $C^{12}C^{13}$  emissions has ever been made, one is tempted to believe that the ratio  $C^{12} : C^{13}$ , while larger than 3 : 1, is sometimes smaller than the terrestrial value, about 100 : 1. However, it must also be large at times, since excellent cometary spectra with over-exposed  $C^{12}C^{12}$  bands sometimes fail to show any trace of  $\lambda 4745$ . A careful quantitative investigation is desirable.

The molecules which have been observed in the coma—OH, NH, CN, CH,  $NH_2$ , ...—are not chemically stable molecules at room temperature. They are radicals, which are physically stable and which will only disappear by photo-dissociation or photo-ionization, not by recombination, since collisions are too infrequent. At least this is true at some distance from the solid nucleus; conditions may be different near the surface of the solids. These radicals result from the photo-dissociation of chemically stable molecules which are evaporated or desorbed from the solid surface: these molecules will henceforth be called "parent molecules". The  $NH_2$  radicals result probably from the photo-dissociation by solar radiation of ammonia molecules liberated from the solids. (However, we do not wish to exclude the possibility that molecules other than ammonia, such as hydrazine  $N_2H_4$ , might play a rôle in the production of  $NH_2$  or NH.) Once evaporated, a  $NH_3$ -molecule has only a limited lifetime: after an average time  $t_0$  it will be either dissociated or ionized by solar radiation.

Example:  $NH_3 + h\nu_{\odot} \rightarrow NH_2 + H$ .

$NH_2$  will also have an average life  $t_1$ , and will next be photo-dissociated or photo-ionized. Series of photochemical transformations take place, such as:



The analogy of such series to the radioactive disintegrations is obvious [45]. The mathematical treatment of the cometary problem proceeds along the classical set of differential equations studied for the radioactive series. If several photochemical effects can take place, such as photo-dissociation and photo-ionization, their relative efficiency should be examined carefully, account being taken of the amount of solar energy available in the different spectral regions. For example, the  $C_2$  molecule may be dissociated at  $\lambda \simeq 2000 \text{ \AA}$ , while ionization requires  $\lambda \simeq 1000 \text{ \AA}$ . It would thus seem that  $C_2$  will much more frequently disappear by dissociation than by ionization.

It is clear that the cometary atmospheres must be treated quite differently from stellar atmospheres. Cometary atmospheres are temporary phenomena. Moreover, the densities are low and no collision takes place; hence the usual equations applied in the study of atomic ionization and molecular dissociation in stellar atmospheres

cannot be employed in the case of comets without great care. Once a molecule has become ionized, there is no chance for it to recapture an electron; similarly recombinations of atoms do not occur. In comets most molecules are on low rotational and vibrational states of the ground electronic level; thus their dissociation and ionization are slowed down in comparison with the laboratory. In all the discussions on cometary molecules the physical data, such as heats of dissociation, ionization potentials, and energy curves, are essential; a good many such data are still lacking.

While it would seem rather probable that the ammonia molecule is the parent molecule for the  $\text{NH}_2$  and  $\text{NH}$  radicals, a great deal of doubt remains for  $\text{OH}$ ,  $\text{CH}$ ,  $\text{CN}$ , etc. One would think of water as parent of  $\text{OH}$ ; but ordinary ice has an extremely low vapour pressure, yet the  $\text{OH}$ -bands are observed at large heliocentric distances. As for  $\text{CH}$ , the methane molecule  $\text{CH}_4$  has been envisaged, especially since methane is found as an occluded gas in meteorites and in terrestrial rocks. However, acetylene  $\text{C}_2\text{H}_2$  may also be plausible. Other molecules which may be envisaged as possible parents are  $\text{HCN}$  and  $\text{C}_2\text{N}_2$ . Neutral  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{N}_2$  must exist and give rise to the tail molecules by ionization.

The chemistry in comet atmospheres is simple and pure photochemistry; no reaction occurs, except possibly near the solid surface. There is no perturbation of the phenomena—such as of the resonance fluorescence—by collision between the molecules. Since radicals are not too easily studied in the laboratory, the comets may eventually furnish valuable data to the physico-chemist.

The three molecules  $\text{CH}$ ,  $\text{CH}^+$ , and  $\text{CN}$  which are present in comets have also been found in interstellar space. On the other hand, the  $\text{C}_2$  molecules which are abundant in comets at heliocentric distances smaller than 2 A.U. have not been observed in interstellar absorption: this absence has been explained satisfactorily [87]. Various theoretical considerations regarding cometary molecules may be applied readily to the interstellar molecules. However, the latter are not necessarily produced by the same mechanism of sublimation or desorption from solids as the cometary molecules. While interstellar  $\text{CH}$  may be formed in certain regions of space by sublimation of grains containing a parent molecule of  $\text{CH}$  [88], it appears that interstellar molecules must also be formed by the association of two colliding atoms with simultaneous emission of radiation. Anyhow a comparison of the physical phenomena regarding cometary and interstellar molecules is instructive. No unidentified interstellar absorption band coincides with an unassigned cometary emission.

Eventually the photometric and spectroscopic observations will provide us with numerical data as to the abundances of the molecules. However, we are still far from this goal. We still lack many values of transition probabilities; little spectrophotometric work has been done; and our information as to the amount of ultra-violet solar radiation which is responsible for the dissociation and ionization of molecules is still very poor. A crude estimate of the mean abundance of  $\text{C}_2$  in a comet head at heliocentric distance 1 A.U. would be  $10^5$  molecules per cubic centimetre; while there is something like 1 molecule of  $\text{CO}^+$  per cubic centimetre in a tail [45]. However, it would be highly hazardous to proceed from these estimates of specific abundances to estimates of the total abundances, since many molecules emit their radiations in unobservable spectral regions. Nevertheless, it is possible to obtain an idea of the maximum total abundances. We have seen that the "vibrational" and "rotational" temperatures were all different, indeed that they had little physical meaning. This

expresses the fact that the densities are so low that the collisions cannot ensure equilibrium conditions. The corresponding upper limit for the total density is of the order of  $10^{10}$  molecules per cubic centimetre [45]. The problem of the densities of matter in the cometary gases has also been studied recently by POLOSOKOV [89].

The atmosphere—head and tail—of a comet is a temporary phenomenon; it must be continuously replenished by liberation of gases from the nucleus. Since the latter has a small mass (hence very little gravitational attraction) all molecules or solid particles that are liberated from the solid fly away freely into space. In no way can a coma be considered as a stable swarm. If the production of gas stopped, the head would disappear in a few hours and the tail in a few days. In the field of solar radiation every molecule has a limited life determined by its possibilities of photo-dissociation and photo-ionization and by the amount of solar energy available in the spectral regions where dissociation or ionization occurs. The CN radicals have certainly a shorter life than the  $\text{CO}^+$ -ions. Indeed, the molecules which are observed in the tail should be considered as highly photo-resistant. The average lifetime of a molecule is proportional to the square of the heliocentric distance. Accordingly the gaseous coma should shrink (but brighten up) in the neighbourhood of the Sun. The latest measurements are those of the extension of the 4050 group in 19481 by JOSE and SWINGS [33]; between 0.9 and 2.2 A.U. this extension varied approximately from 4100 km to 22,000 km, *i.e.* in a ratio 1 : 5.3 which may be compared to the squares of the heliocentric distances 1 : 6. A "dust head" would, of course, not shrink in the same way as a "gaseous head". At large distances where the heads are probably made up mostly of solid particles the diameters should not change much in normal conditions (*i.e.* assuming no change in solar excitation and in the structure of the solids), although the brightness would. Of course, if a part of a distant coma is due to polyatomic molecules, it should show the same type of shrinkage proportional to  $r^2$  as a gaseous head near perihelion.

What is the physical meaning of the extension of molecules within the head or the tail? [45] [70] [90]. Suppose that the molecules are produced in a point source. Let us assume that no electrodynamic effect takes place in the head. The average extension will be the product of the average velocity by the average lifetime. The velocity is the summation over five factors: the thermal velocity ( $v_t$ ), the velocity imparted in the process of photo-dissociation of the parent molecule ( $v_a$ ), the velocity acquired in an ionization process ( $v_i$ , for ions only), that due to radiation pressure ( $v_r$ ), and that due possibly to some kind of eruption phenomenon ( $v_e$ ).  $v_t$  corresponds to the temperature of the nucleus and is very small.  $v_a$  results from the conversion of solar energy, in excess to that required for dissociation, into kinetic energy; laboratory experiments [91] have shown that  $v_a$  is of the order of 1 or 2 km per sec., *i.e.* of the order of the velocities in cometary atmospheres [92].  $v_a$  exists, of course, only for molecules resulting from the photo-dissociation of parent molecules, not for ions such as  $\text{CO}^+$ ,  $\text{N}_2^+$ ,  $\text{CO}_2^+$ , if the latter result directly from the ionization of the chemically stable molecules CO,  $\text{N}_2$ , and  $\text{CO}_2$ . For  $\text{CO}^+$ ,  $\text{N}_2^+$ ,  $\text{CO}_2^+$ , we should consider the  $v_i$  component, which is certainly small since the electron collects most of the remaining energy. In the head the radiation pressure does not play the dominant rôle that it plays in the tail: for the main molecules of the head, CN and  $\text{C}_2$ , the radiation pressure does not exceed appreciably the solar gravitational attraction.

The radiation pressure acts efficiently on the molecules of the tail. Moreover, BIERMANN [93] has shown recently that the ionized molecules of the tails are strongly

affected by the impact of ionized solar corpuscular streams, the effect of which may exceed considerably the effect of radiation pressure. That comets are influenced by solar phenomena appear more and more probable, as was shown by various investigators, especially by M. BEYER [94]. As OORT expressed it in his Halley Lecture for 1951 [95]: "Comets may ultimately be used as test objects around the Sun, by means of which more complete information regarding solar eruptions may be recorded". However, a discussion of this topic falls outside the scope of the present paper.

The parent molecules are liberated from the solid nucleus, either by desorption or by sublimation. WHIPPLE [96] has recently developed an "icy conglomerate model" for comet nuclei which appears to account satisfactorily for the anomalous acceleration or deceleration in the mean motions of certain comets (due to a "rocket-effect") [97]. This model helps greatly also in understanding several physical phenomena related to the formation and evolution of the cometary atmospheres. In WHIPPLE's theory the ices of compounds of H, C, N, and O contain a mass of dust containing the elements usually present in the silicate and metal phases of meteorites. When the ices evaporate at small heliocentric distances, the dust would form an insulating layer over the more volatile compounds. Evidence is accumulating that nearly all (if not all) the meteors derive from comets [97a]; the spectra of meteors show the presence of Na, Fe, Ni, Cr, Ca, Mn, Mg, Si, and Al. WHIPPLE's comet model is rather similar to that postulated by H. C. UREY for the formation of planetesimals [97b].

Difficulties with WHIPPLE's model arising from the fact that the vapour pressures of solid  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ , etc., differ by large factors may be overcome by assuming the presence of solid hydrates [98], since the latter have rates of sublimation of the same order of magnitude.

Na-lines are observed at such heliocentric distances where the temperature of the solids is still so low—very much lower than the boiling-point of sodium ( $877^\circ\text{C}$ )—that neither vapour pressure from the solid state nor probably desorption would be likely to produce the required amount of Na-vapour [99]. If, however, Na-atoms or molecules containing Na are imbedded in ices the sublimation of the latter followed by the photo-dissociation of the molecules could release the sodium atoms. The resonance lines of K ( $\lambda 7664.9$  and  $\lambda 7699.0$ ) should eventually also be observed at small distances from the Sun.

At large heliocentric distances the coma which has a continuous spectrum [100] is probably caused by the sublimation of very volatile gases, which are invisible themselves, but blow meteoric dust from the nucleus.

The theory of sublimation from ices has been criticized recently, especially by RIJVES [101], who favours the old theory of desorption [102] (gradual emission of occluded gases by the surface of the heated solid nucleus). The problem of the heating of the solid nucleus, taking into account the heat conductivity, has been treated by MINNAERT [103] and by LEBON [104]. The chemical reactions which may take place between radicals or molecules at the cold surface of the nucleus [98] have never been studied. Indeed, many problems of cometary physics and chemistry which are closely related to cryoscopy remain untouched. These matters will not be discussed in the present paper which is limited to the spectra of comets. Neither will the problems of the origin and evolution of the comets, the relations of comets to meteorites, or the structures of the tails be envisaged [105]; see also footnote on p. 949.

Despite the considerable progress made in recent years in the field of cometary spectra and related matters, much remains to be done. The efforts of the patient observers who endeavour to discover new comets [106] should be encouraged, since we need many new photometric and spectroscopic observations.

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