

## Molecular Bands in Cometary Spectra. Identifications

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SPECTRA of comets have been observed from  $\lambda 3000$  to  $\lambda 6600$  approximately; some observations have also been made beyond  $\lambda 6600$ , but they are only of a preliminary character, and they do not provide any reliable identifications. Even the yellow and near red regions are relatively poorly known. The reason is that modern grating spectrographs have not yet been used to investigate comets, and there is no doubt that this is the most important observation needed at the present time to improve our knowledge of cometary physics. We may certainly expect that the region  $\lambda > 6000\text{A}$  of cometary spectra will reveal new molecules—even probably atoms, such as potassium, when the comet is in the neighborhood of the sun. In the spectral range explored, only low dispersion spectrograms have been obtained as yet, the sharpest projected slit width at  $\lambda 4000$  having been of the order of  $0.7\text{A}$ .

The following molecules have been identified in comets: OH, NH, CN, CH,  $\text{C}_2$ ,  $\text{CH}^+$ ,  $\text{CO}^+$ , and  $\text{N}_2^+$ . Some of these identifications (OH, NH,  $\text{CH}^+$ ) are quite recent, and have been made mainly on the basis of spectroscopic material obtained at the McDonald Observatory since 1940.<sup>1</sup> The molecules have definite distributions in the cometary atmosphere, some, like CH, being concentrated very close to the nucleus, while others, like  $\text{C}_2$  or CN, extend all over the head. The tails are mainly characterized by  $\text{CO}^+$  and  $\text{N}_2^+$ , also by  $\text{CH}^+$  in the neighborhood of the nucleus. Besides the well-identified molecular bands, there still remain unidentified spectroscopic features, that I shall discuss in the course of this report: in order to avoid observational material of doubtful character, or wavelengths of very low precision, the discussion will be concerned only with the unidentified emissions of the blue, violet, and ultraviolet regions.

<sup>1</sup> Swings, Elvey, and Babcock, *Astrophys. J.* **94**, 320 (1941) (Comet 1940c) and **95**, 218 (1942) (Comets 1941c and 1941d); D. M. Popper and P. Swings, *Astrophys. J.* **96**, 156 (1942) (Comet 1942a); P. Swings, *Lick Obs. Bull.* **19**, 131 (1941); P. Swings, *Astrophys. J.* **95**, 270 (1942); P. Swings, *Pub. Astronom. Soc. Pac.* **54**, 123 (1942).

Besides the molecular bands (and the Na lines at small heliocentric distances), all the spectra of comets show a solar absorption spectrum which is evidently due to the reflection or scattering of solar light. For a specific solar excitation, i.e., at a specific heliocentric distance  $r$ , the intensity ratio of the solar spectrum and of the emission bands varies considerably from comet to comet, as do also to a certain extent the relative intensities of bands emitted by various molecules. For example, the relative intensities of the bands emitted by the carbon compounds CN, CH, and  $\text{C}_2$  may differ for different comets observed at the same heliocentric distance  $r$ . This means that the chemical constitution of the cometary gas varies to some extent from comet to comet. Such variations occur also among the occluded gases found in the different types of iron or stone meteorites by breaking or heating them in vacuum. It is well known that the gas released by meteorites may sometimes amount to sixty times the volume of the meteorite itself. The gases which have been found in meteorites are  $\text{CO}_2$ , CO,  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ; the ratio of abundance of  $\text{CH}_4$  and CO (or  $\text{CO}_2$ ), for example, is very different in stone and in iron meteorites.<sup>2</sup> It is perhaps not entirely legitimate to assume for cometary nuclei a chemical constitution similar to that of the meteorites found on the earth. Yet as a working hypothesis, it may help to relate the different gaseous constitutions of cometary atmospheres to the different chemical natures of the occluded gases in the various types of meteorites.

From the beginning of the spectroscopic observations of cometary spectra, it has been noticed that, except for the Swan bands of  $\text{C}_2$  which have an appearance similar to that obtained in the laboratory, all the other bands show a peculiar distribution of intensity among the rotational and vibrational transitions. In all the cometary molecules which have a permanent

<sup>2</sup> See, for example, G. P. Merrill, *Proc. Am. Phil. Soc.* **65**, 119 (1926); also H. von Klüber, *Das Vorkommen der Chemischen Elemente im Kosmos* (Leipzig, 1931).

electric dipole—hence except for  $C^{12}C^{12}$ —only the lines arising from the first rotational levels are observed:

$$K' \leq 3 \text{ for OH; } \leq 2 \text{ for NH; } \leq 6 \text{ for CH;} \\ \leq 2 \text{ for CH}^+; \leq 25 \text{ for CN.}$$

But as is shown in Dr. McKellar's report, the intensity distributions among these lines of low rotational quantum number deviate considerably from smooth, low temperature distributions of the Boltzmann type. The peculiar intensity distributions result from the mechanism of excitation and from the distribution in the rotational levels of the ground electronic state. Recent investigations which have just been discussed by Dr. McKellar have shown that the presence of absorption lines in the exciting solar radiation reduces the intensities of certain rotational transitions relative to the others. As for the rotational distributions of population in the ground electronic state, they also differ from the Boltzmann type. This evidently complicates the identification work in many cases. Even in the CN bands, the attribution of the various observed maxima to the proper rotational and vibrational transitions could not be made with certainty until quite recently. For various comets observed at the same heliocentric distance, the rotational intensity distributions may differ if the radial velocity shift of the exciting solar radiation is different. And similarly a comet observed at various heliocentric distances may show different rotational intensity distributions. In both cases the variations are due to the differences in exciting radiation brought about by the Doppler shift, and to the differences in rotational distribution in the ground electronic state. Such variations have been observed, especially in the OH and CN bands.

The real procedure in identifying cometary emissions should thus be the decomposition of the exciting radiation into a number of monochromatic excitations. The observed pattern is the superposition of resonance doublets (or singlets or triplets according to the type of electronic transition), each consisting of a  $P$  and a  $R$  line, and each having a specific intensity. And we should thus not expect the pattern to

resemble closely the intensity distribution in a laboratory spectrum, even at low temperatures.

The problem of the excitation of cometary fluorescence by solar radiation which differs considerably from a blackbody continuum fits into the general astronomical problems of fluorescence excitation, at present under investigation at the McDonald and Yerkes Observatories. In every astronomical case of fluorescence excitation, the exciting radiation is different from a blackbody continuum: there are always either absorption lines, bands or continua, or emission features, and the absorption or emission lines of the exciting radiation are shifted to a certain extent with respect to the excited gas, because of relative velocities.<sup>3</sup>

<sup>3</sup> Typical examples of such fluorescence are the following: (a) Specific incomplete multiplets of O III and N III may be excited in nebulae and similar objects, due to the coincidence of the resonance line of He II with an absorption line of O III, and another similar coincidence between O III and N III lines (Bowen's mechanism). The efficiency of this mechanism depends largely on the velocities of the layers emitting the He II spectrum, relative to the layers containing the  $O^{++}$  ions. Coincidences appearing more or less suddenly in the course of the evolution of a nova will enhance the O III and N III incomplete multiplets suddenly. (b) In shells surrounding stars of early type, peculiar selectivities are observed among the transitions in He I (variations in relative intensities of the triplets and singlets in emission), N III (presence of  $3p^2P^0 - 3d^2D$  in emission, while  $3s^2S - 3p^2P^0$  is present in absorption), C III (presence of  $3p^1P^0 - 3d^1D$  in emission, while  $3s^2S - 3p^2P^0$  is in absorption), N IV (same as C III), Si III (all the transitions whose lower levels are  $4p^1P^0$  and  $4p^3P^0$  appear in emission; conversely the lines whose upper levels are  $4p^1P^0$  and  $4p^3P^0$  are present in absorption only), Si II (absence of the usually strong doublet  $3d^2D - 4f^2F^0$ ), N II, C II, Fe II, etc. . . . In the shells of lowest excitation (late Be and Ae stars), the Balmer lines themselves are excited by fluorescence. The underlying stellar radiation is considerably depleted beyond the Lyman limit, which reduces considerably the ionization of the hydrogen atoms in the shell, and consequently the recombination mechanism. As for the fluorescence excitation of the Balmer lines, its efficiency will be affected by the presence of Lyman absorption lines in the exciting radiation; this efficiency depends on the velocity and density distributions of the hydrogen atoms of the shell, and on the profile of the absorption lines of the exciting radiation; any variation in these factors will give rise to changes in intensity and profile of the Balmer emission lines. (c) In nebulae excited by nuclei possessing absorption or emission lines, these features affect the excitations, ionizations, and recombinations to an observable extent. (d) The anomalous selectivities observed among certain emission lines in long period variables are probably due also to the presence of emission or absorption features, especially molecular bands, in the exciting radiation.

Evidently we may generalize, and instead of considering the excitation only, we may discuss the atomic and molecular ionization and the molecular dissociation mechanisms in a field of diluted radiation which is not of the blackbody type. A number of applications are then of interest: the spectra of novae (for example, the appearance of molecular bands in these "too hot" atmospheres), the ioniza-

The identifications of OH, NH, CH, and CH<sup>+</sup> bands do not present any real difficulty. The case of OH<sup>+</sup> is complex, since the (0,0) band of the <sup>3</sup>Π→<sup>3</sup>Σ system of OH<sup>+</sup> falls in the same spectral region as the fairly strong Δ*v*=+1 sequence of CN. Moreover, the exciting solar spectrum has a very complex profile between λ3565 and λ3590, because of the presence of a number of very strong Fraunhofer lines. It does not seem possible to explain the cometary fea-

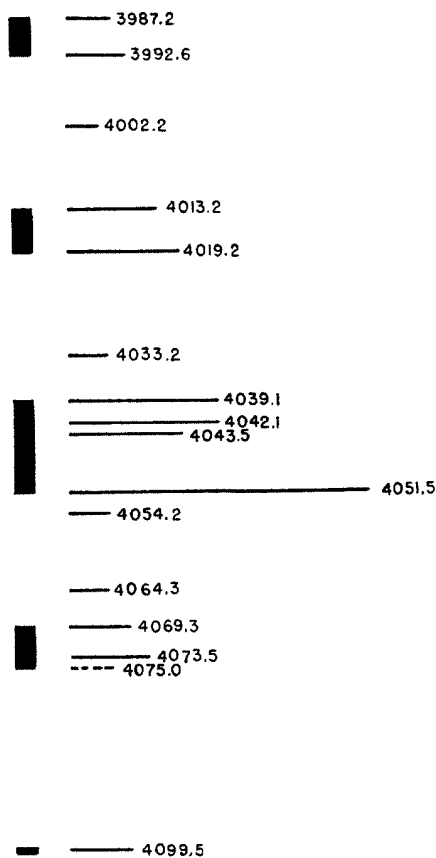


FIG. 1. Diagram of the λ4050 group.

tures observed near λ3570 on the basis of CN and CO<sup>+</sup> only; yet a better resolution than heretofore available is required before we can be certain of the identification of OH<sup>+</sup> in comets.

tion of interstellar atoms, and the dissociation and ionization of interstellar molecules, the abnormal intensities of absorption lines in peculiar *A* stars (for example, the strength of the Eu II lines and the weakness of the Ca II lines in α<sup>2</sup> Canum Venaticorum), the general problem of the molecular abundances in late-type stars and the subdivision into TiO, ZrO, and carbon sequences of cool stars, etc. . . .

Certain comets have revealed, besides the Swan bands of C<sup>12</sup>C<sup>12</sup>, also the Δ*v*=+1 sequence of C<sup>12</sup>C<sup>13</sup> at λλ4745, 4723, and 4706. These bands of C<sup>12</sup>C<sup>13</sup> are hazy, whereas the C<sup>12</sup>C<sup>12</sup> bands have sharp edges. A different rotational intensity distribution for C<sup>12</sup>C<sup>12</sup> and C<sup>12</sup>C<sup>13</sup> may be understood: whereas the highly excited rotational levels of the ground electronic state of C<sup>12</sup>C<sup>12</sup> can be "depopulated" only by quadrupole emission (in the far infra-red pure rotation spectrum), a dipole mechanism of greater probability (although still intrinsically small) operates for C<sup>12</sup>C<sup>13</sup>.

By far the most puzzling group of unidentified features is a group of strong lines near λ4050. Many elaborate discussions have been published on this group which, at times, was attributed to CH (Raffety band), C<sub>2</sub> (Deslandres-d'Azambuja system <sup>1</sup>Π→<sup>1</sup>Π), CN (tail bands), NaH, etc. . . . None of these attempts has given a satisfactory solution. We may summarize the astronomical situation as follows.<sup>4</sup> A report on the physical side of the problem is given by Dr. Herzberg in his report.

#### OBSERVATIONAL DATA CONCERNING THE λ4050 GROUP

It consists of a strong, fairly sharp line at λ4051.5, accompanied by weaker lines on either side (see Fig. 1). This group is observed in the central parts of the coma, more or less concentrated near the nucleus, although not quite as much as the CH lines. When observed with a dispersion of 55Å/mm and an effective slit width of 0.8Å, all the lines are fairly sharp. The lines are not observed in any late-type star, which indicates that they do not belong to a normal molecule consisting of two abundant atoms. None of these lines has ever been observed in interstellar absorption.

In a general way, we may say that the intensity ratio (int. 4050)/(int. CH) increases with the heliocentric distance, the average situation being: int. 4313 (CH) > int. 4051 for *r* < 0.8, while the opposite is true for *r* > 0.8. At large heliocentric distances, the CH band is very weak relative to λ4051. This behavior is illustrated in Table I. In Comet Cunningham whose spectrum

<sup>4</sup> P. Swings, Pub. Astronom. Soc. Pac. 54, 123 (1942).

was observed from  $r=1.2$  to  $r=0.5$ , the ratio (int. 4050)/(int. CH) decreased steadily with  $r$ .

There are also individual characteristics of specific comets. In Comet Morehouse ( $r \approx 0.94$ ), the  $\lambda 4050$  group was extremely weak, while CN and  $C_2$  were very intense; but CH was also absent.

#### GENERAL CONCLUSIONS REGARDING THE IDENTIFICATION OF THE $\lambda 4050$ GROUP

Let us first consider the case of a diatomic emitter. In order to give sharp lines with a dispersion of 55A/mm, the diatomic molecule must be a hydride. All the diatomic hydrides (neutral and singly ionized) of the light elements are known, except  $NH^+$ . Anyway, the emitter cannot be a neutral hydride, otherwise it would have been found in late-type stars. If the emitter is  $NH^+$  which is isoelectronic with CH, the strongest system should be a  ${}^2\Delta \rightarrow {}^2\Pi$  transition; in this case,  $\lambda 4051.5$  should be a blend of the first lines of the  $Q$  branch;  $\lambda 4043.5$  and  $\lambda 4042.1$  would correspond to  $K=1$  in the  $R_1$  and  $R_2$  branches;  $\lambda 4039.1$  would correspond to  $R_1+R_2$ ,  $K=2$ . Lines to the red of  $\lambda 4051$  would belong to the  $P$  branch. As for the lines to the violet of  $\lambda 4039$ , their attribution is uncertain. The  $B''_0$  value obtained turns out to be 13 or 14  $cm^{-1}$ , as compared with  $B''_0(NH) = 16.33 cm^{-1}$ .

Several objections to this identification arise. The reduction of  $B''_0$  when passing from NH to the hypothetical  $NH^+$  is rather larger than would be expected from a plot of the  $B''$  values of ionized and neutral molecules.<sup>5</sup> The spectrum of  $NH^+$  should also be expected a little more to the red.<sup>6</sup> The matter of intensities is discussed in Dr. Herzberg's report. If the  $\lambda 4050$  group is due to  $NH^+$ , the oscillator strength  $f(NH^+)$  must be large, and it seems strange that no line of this group has ever been observed as an interstellar absorption line in adequate stellar spectra. Finally it is strange that the intensity of  $NH^+$  lines would increase with heliocentric distance.

Next we must consider the possibility of polyatomic molecules, especially of the simple

ones consisting of the cosmically abundant atoms H, C, N, and O, and resulting from the photo-dissociation of the chemically stable polyatomic compounds found in meteorites.<sup>4</sup> In this direction, Dr. Herzberg has recently suggested that the group may be a  $\perp$  band of a nearly symmetric top molecule, the observed series of bands (tentatively indicated in Fig. 1, but this classification may have to be modified) corresponding to the subbands. The corresponding molecule can only be  $CH_2$  or  $NH_2^+$ , and  $CH_2$  is more likely. Actually Dr. Mulliken had predicted last year the existence of an electronic transition of  $CH_2$  in the region 4000–4500A.<sup>7</sup>

From the astronomical point of view,  $CH_2$  is an excellent suggestion, because we should then understand easily why the intensity ratio of  $\lambda 4051$  and  $\lambda 4313$  (CH) increases with heliocentric distance, why the band is absent in the late-type stars, and why we do not find it in interstellar space. Since CH results from the photo-dissociation of some saturated parent molecule, we may expect  $CH_2$  to be formed together with CH, or as an intermediary stage.

The last word is evidently left to the labora-

TABLE I. Relative behavior of  $\lambda 4051$  and  $\lambda 4313$  (CH) in various comets.

Comet	Heliocentric distance	$\lambda 4051$	$\lambda 4313$
Beliavsky	0.33	very weak	strong
1910 I	.47	weak	strong
Brooks	.49	moderate	strong
Cunningham	.52	moderate	strong
Cunningham	.71	strong	strong
Cunningham	.85	strong	fairly strong (<4051)
Cunningham	.99	strong	moderate
Pons-Winnecke (in 1927)	1.0	strong (>CN)	moderate
Delavan	1.20	strong	absent
van Gent	1.25–1.51	strong	very weak
Mellish	1.57	strong	very weak
Whipple	1.5–1.8	strong	hardly visible

tory spectroscopist. What we may simply conclude from this discussion is that  $NH^+$  is the only diatomic possibility which is left, but that it is not too promising. As for possible polyatomic emitters,  $CH_2$  is very promising, from the astronomical as well as from the physical point of view. Whether the observed intensity distribu-

<sup>5</sup> A. E. Douglas and G. Herzberg, Can. J. Research 20, 71 (1942).

<sup>6</sup> Private communication of Dr. Herzberg (from a plot of the frequency differences between corresponding band systems of ionized and neutral molecules against the atomic number).

<sup>7</sup> P. Ledoux, Pop. Astronom. 49, 513 (1941). (Summary of the symposium on interstellar lines at the Yerkes Observatory, on June 30, 1941.)

tion can be obtained by excitation of CH<sub>2</sub> molecules by solar radiation will have to be investigated.

The exact nature of the parent molecules and the dissociation and ionization mechanisms are still practically unexplored. The ionization potentials and the corresponding wave-lengths are:

for CO,	14.1 ± 0.2 v,	or	λ880;
for N <sub>2</sub> ,	15.51 v,	or	λ800;
for CH,	11.13 ± 0.22 v,	or	λ1110.

A direct photo-ionization of CO, N<sub>2</sub>, and CH by solar radiation appears very improbable. If the sun radiates like a blackbody at  $T \approx 6000^\circ\text{K}$ , its continuum must be very weak around  $\lambda 1000$ . Besides, the situation is even worse because the Lyman absorption continuum setting in at  $\lambda 912$  must be extremely strong. Hence we should expect the amount of solar energy available for  $\lambda < 880\text{\AA}$  and  $\lambda < 800\text{\AA}$  to be extremely small, even, in fact, if the continuous photospheric spectrum would otherwise be much richer than a blackbody at  $T \approx 6000^\circ\text{K}$ . As for CH, its ionization limit falls about half-

way between Lyman  $\alpha$  ( $\lambda 1216$ ) and Lyman  $\beta$  ( $\lambda 1026$ ), which must be strong in the solar spectrum and have extensive wings. Excitation by impacts of solar electrons, such as we observe in the aurora borealis, may occasionally influence the ionization in comets, but is probably not the permanent source of ionization. Photo-dissociations of parent molecules into a positive and a negative ion are not excluded, but there is probably little we could say about it at the present time. Finally ionization in several steps, via intermediate (possibly metastable) levels of CO, N<sub>2</sub>, and CH may play a role.

The general conclusion of this report is obvious: many questions remain to be answered before we could reach a clear understanding of the physical chemistry of comets. The help of the physicists is especially desirable for the investigation of the spectra of NH<sup>+</sup>, CH<sub>2</sub>, CN<sup>+</sup>, C<sub>2</sub><sup>+</sup>, and for the determination of additional  $f$  values which would make possible an estimation of the molecular abundances. Additional observations are also required in a number of fields, but especially spectroscopic observations in the red and near infra-red regions.