

REPORTS ON THE PROGRESS OF ASTRONOMY

COMETARY SPECTRA

For many years the only molecules identified in comets have been CN , C_2 , CH , CO^+ and N_2^+ : CN , C_2 and CH belong mainly to the head of the comets, whereas CO^+ and N_2^+ are characteristic of the tail. In the last three years four additional molecules have been shown to be present in the head, three of them diatomic (OH , NH , CH^+), and one triatomic (CH_2); it is also highly probable that OH^+ and NH_2 are present. These additions result from improved observations, especially in the ultraviolet region, and from recent laboratory work. Only a very few weak emission features remain unidentified in the region $\lambda < 4800 \text{ \AA}$., but there are still a number of fairly strong unexplained emissions in the visual region, some of which are being tentatively attributed to NH_2 .

Most cometary bands display rotational structures which depart considerably from the rotational intensity distributions of molecular bands as obtained from sources in the laboratory, even at low temperatures. These departures have been successfully attributed to the mechanism of excitation by solar light, account being taken of the presence of Fraunhofer lines. On the basis of these new data, interesting conclusions can be reached on certain general problems of cometary physics, although many major questions remain open. The present review discusses the progress made during the last three years in the spectra of the heads of comets. No important spectroscopic contribution has been made to the problem of the tails, except the presence of CH^+ which will be mentioned later on.

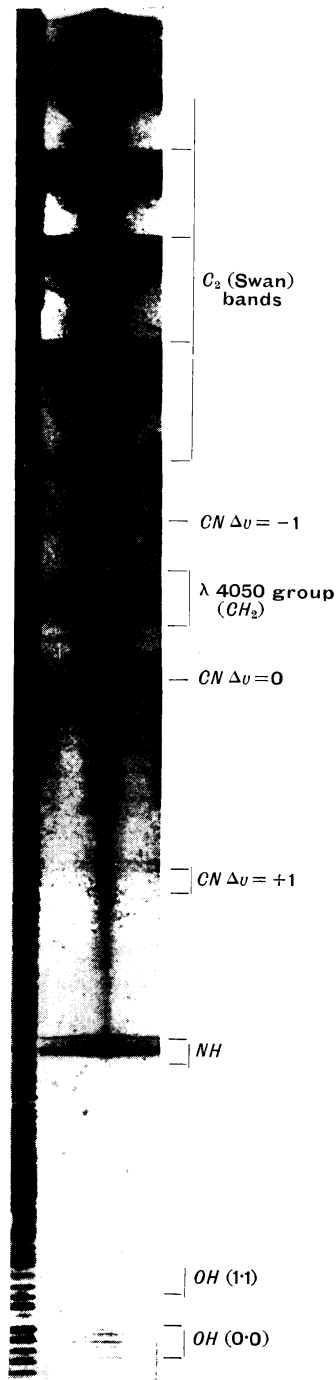
1. *New Observations and Identifications in the Ultraviolet Region (1)*

Up to 1940 the cometary emissions in the ultraviolet region, $\lambda < 3500 \text{ \AA}$., had been photographed only with spectrographs of very low resolving power, and no reliable identification could be based on these observations. Since 1940 the ultraviolet spectra of many comets have been obtained at the McDonald Observatory with two quartz slit spectrographs having the respective dispersions 137 and 69 $\text{\AA}/\text{mm}$. at $\lambda 3360$. This material has revealed the presence in most comets of two fairly strong groups of lines: one near $\lambda 3090$ due to OH , the other near $\lambda 3360$ due to NH . Moreover, fainter lines due to OH (possibly with a weak contribution of CH), appear near $\lambda 3140$ (six lines of the 1, 1 transition of OH) and $\lambda 3204$ (two lines of the 2, 2 transition). In the region of longer wave-lengths, the $\Delta v = +1$ sequence of CN gives a characteristic group near $\lambda 3570$, which group very probably contains a contribution from OH^+ . These features are shown on Plate 2.

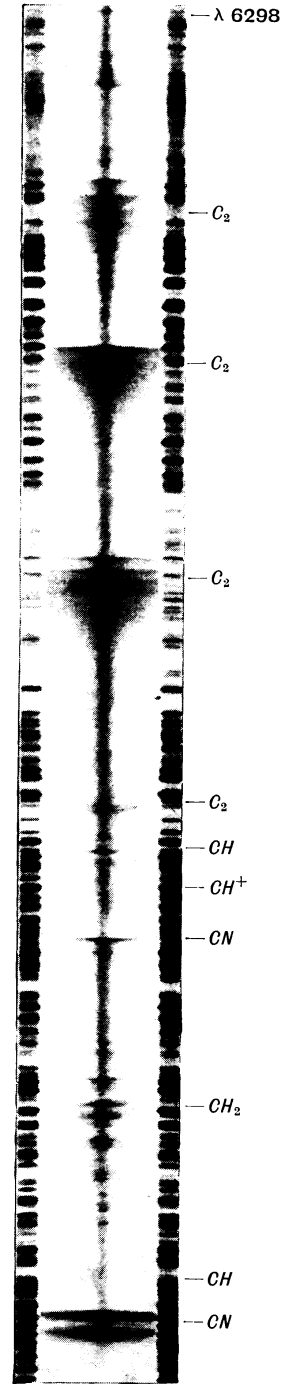
OH-lines.—The (0, 0) band of the ${}^2\Sigma^+ \rightarrow {}^2\Pi_{1nv}$ system of OH consists of several sharp lines in the region $\lambda\lambda 3078\text{--}3100$; the wave-lengths as measured in Comets 1940 *c* (Cunningham), 1941 *d* (van Gent) and 1942 *a* (Whipple) are given in Table I. It appears from this table that the relative intensities of the OH lines vary appreciably from comet to comet (see section 4).

The *R* branches are absent, except for the first lines $R_2(\frac{1}{2})$ and $R_2(1\frac{1}{2})$ at $\lambda 3084.03$ and $\lambda 3080.22$ which, on microphotometer tracings, appear in the violet wings of $P_1(2\frac{1}{2})$ at $\lambda 3086.3$ and $P_1(1\frac{1}{2})$ at $\lambda 3081.6$.

The six faint lines observed in comet 1940 *c* between $\lambda 3134.5$ and $\lambda 3152.4$ (Plate 2) belong to the (1, 1) band of OH , and possibly to the (0, 0) Fortrat band of $CH(c^2\Sigma^+ \rightarrow x^2\Pi)$.

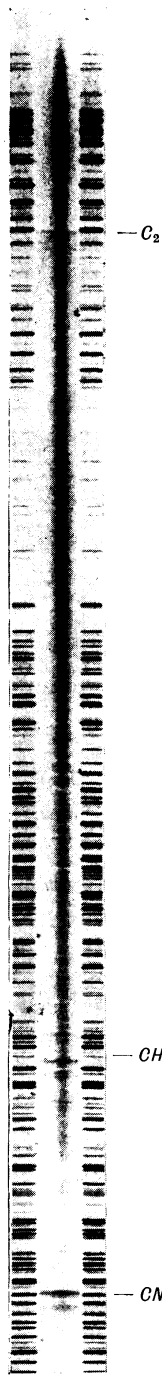


Spectrum of Comet Cunningham (1940 *c*) in the region λ 3000- λ 6300.

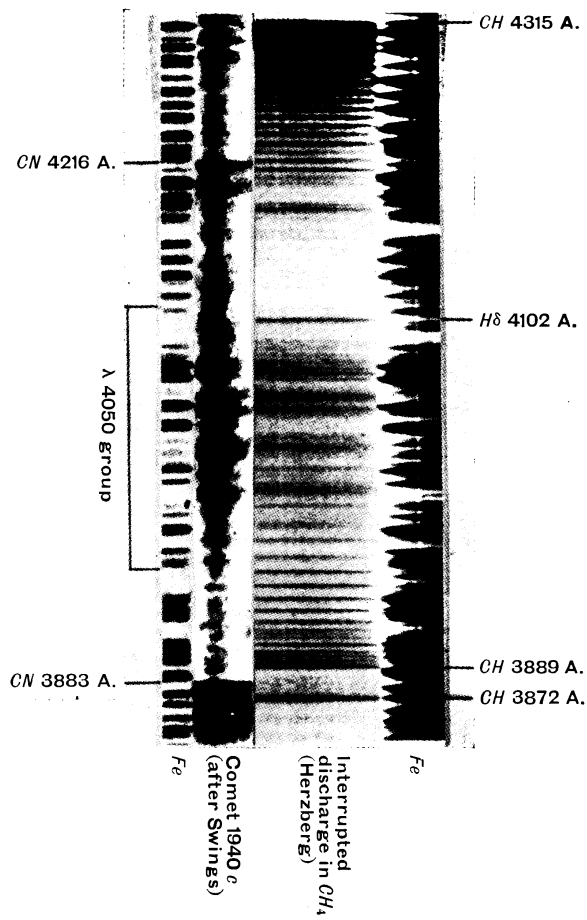


Spectrum of Comet Cunningham (1940 *c*) in the region λ 3850- λ 6300.

P. Swings, Cometary Spectra.



Spectrum of Comet 1942 α (Whipple) in the region λ 3850- λ 5700, on a perfectly moonless night.



Identification of CH_2 in Comet Spectra.

P. Swings, Cometary Spectra.

TABLE I
(o, o) Band of OH in Comets 1940 c, 1941 d, and 1942 a

1940 c		1941 d		1942 a		λ Lab.	Notation
2	3078.5	1-0	79.0	1-0	78.7	78.43	$Q_1(1\frac{1}{2})$
1	3081.6	3	81.7	4	81.9	81.64	$P_1(1\frac{1}{2})$
2	3086.3	1-2	86.3	86.38	$P_1(2\frac{1}{2})$
4	3090.3	1	90.2	0	89.7	90.46	$Q_2(\frac{1}{2})$
						89.84	$Q_2(1\frac{1}{2})$
						89.84	$Q_2(2\frac{1}{2})$
1	3093.7	2	93.6	2	93.9	93.72	$P_2(1\frac{1}{2})$
3	3096.4	96.34	$P_2(2\frac{1}{2})$
2	3099.4	0	99.4	99.57	$P_2(3\frac{1}{2})$

NH lines.—The (o, o) band of the $^3\Pi \rightarrow ^3\Sigma$ system of NH consists of a group of seven strong lines near λ 3360. Their wave-lengths are listed in Table II.

TABLE II
(o, o) Band of NH in Comet Cunningham ($^3\Pi \rightarrow ^3\Sigma$)

Comet	Laboratory	Notation	Comet	Laboratory	Notation
3350.8 (2)	50.8	$R_2(1)$	3361.5 (2)	61.73	$Q_1(1)$
3354.1 (4)	53.92	$R_2(0)$		61.0	$Q_1(2)$
	53.64	$R_1(1)$	3364.7 (2)	64.0	$P_2(2)$
3357.9 (8)	57.83	$R_1(0)$	3369.1 (3)	69.1	$P_1(2)$
	57.8	$Q_2(2)$	3372.0 (1)	72.1	$P_1(3)$

Region $\lambda\lambda$ 3560–3600.—A group of lines observed around λ 3570 presents a complex problem. There is no doubt that the major part of the emission belongs to the $\Delta v = +1$ sequence of CN; yet certain features are certainly not attributable to CN. The (o, o) band of $OH^+(^3\Pi \rightarrow ^3\Sigma)$ falls in the same region, and so does the (8, o) band of CO^+ . The lines measured around λ 3570 in the spectrum of comet 1940 c are listed in Table III with their identifications.

TABLE III
Lines Observed in Comet 1940 c between λ 3560 and λ 3600

Comet		Element	Identification *	
λ	Int.		Notation	
			Vibrational	Rotational
3565	1-0	? OH^+	(o, o)	$R_3 \dagger$
3572.2	2	$\left\{ \begin{array}{l} CN \\ OH^+ \end{array} \right.$	(1, o)	$R(14) \ddagger$
			(2, 1)	$R(5) \ddagger$
3577.3	1-2	$\left\{ \begin{array}{l} CN \S \\ CN \S \end{array} \right.$	(o, o)	$Q_3(1) + Q_3(2)$
			(1, o)	$R(5) \ddagger$
3584.3	2-3n	CN	(2, 1)	$P(5) \ddagger$
			(1, o)	$P(2)-P(14)$
3589.4	1-0	$CO^+ \S$	(8, o)	...
3597.4	1-2 ¶	$CO^+ \S$	(8, o)	...

* Contributions by the bands of NO (β system), N_2 (second positive system), N^+ (first negative system), and C_2 (Deslandres-D'Azambuja system) that fall in this region may be disregarded.

† $R_3(1), R_3(2), R_3(3), R_3(4)$.

‡ Blend of lines around this transition.

§ Minor contribution of OH^+ not excluded.

|| Extending from λ 3581.4 to λ 3586.3.

¶ Possibly double at λ 3595.7 and λ 3598.6.

As is apparent from this table, the situation is rather confused. This is mainly because the McDonald Observatory spectrograms, which have the correct exposure around λ 3570, have a dispersion of only 175 A./mm. and an effective slit width of 2.5 A. in this region. The line λ 3572.2 is definitely too strong to be due only to $R(14)$ of (1, 0) and $R(5)$ of (2, 1), and a contribution by OH^+ is very likely. As for λ 3565, it does not seem possible to attribute it to $R(17)$ of the (2, 1) band of CN , and it is more probably due to the first lines of the R_3 branch of OH^+ .

The lines λ 3589 and λ 3597 were enhanced on the spectrogram of Comet Cunningham, taken on 1941 December 28, on which the tail spectrum was well apparent; this exposure is the only one obtained of Comet Cunningham at the McDonald Observatory, showing all the strong bands of CO^+ and N_2^+ . It is thus safe to attribute λ 3589 and λ 3597 mainly to the (8, 0) band of CO^+ , which has a laboratory intensity of 6 on a scale of 1-10; but OH^+ may be a contributor to these features.

Summarizing the present situation, we may say that there is a strong suspicion that the (0, 0) band of OH^+ is present in cometary spectra. The fainter (1, 0), (0, 1) and (1, 1) bands near $\lambda\lambda$ 3332, 3893 and 3695, respectively, have not been observed in comets. It is desirable to have observations of cometary spectra in the region around λ 3570 with a higher resolving power.

2. New Observations and Identifications in the Photographic Region

Cyanogen bands.—The four sequences $\Delta v = 1, 0, -1$ and -2 of the violet system $^2\Sigma^+ \rightarrow ^2\Sigma^+$ have been observed and described on many occasions. Special emphasis

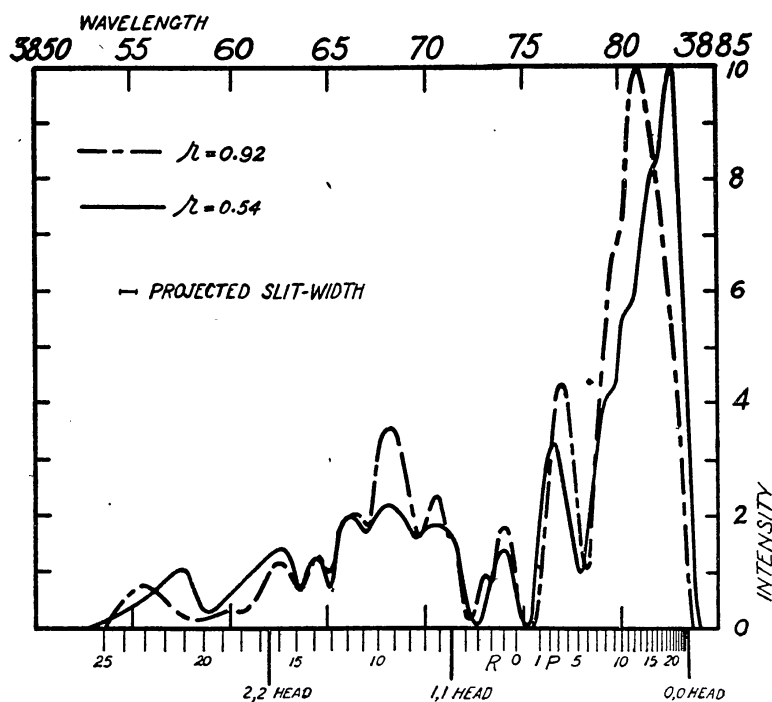


FIG. 1.—Observed CN band profiles, Comet 1940 c, $r = 0.54$ and 0.92 .

has been placed in recent years on the intensity distributions, which differ considerably from the laboratory intensity distributions even at low temperatures. Instead of having a smooth profile, as is usually found in the laboratory sources, the CN bands of comets present complex structures with fairly sharp maxima and minima. Such structures have been observed in all sequences whenever the resolving power of the spectrograph was high enough (2). Fig. 1 gives the profile of the $\Delta v = 0$ sequence as observed by McKellar in Comet Cunningham. The most striking feature, which is also apparent

on Plates 3 and 4, consists in two maxima near $P(3)$ and $R(1)$, followed by deep minima around $P(5)$ and $R(3)$. For comets 1941 *e* (3) (Paraskevopoulos-de Kock), 1942 *a* (4) (Whipple 1) and 1942 *f* (5) (Whipple 2), spectrograms of effective slit width 0.7 Å. reveal some structure in the maxima near $P(3)$ and $R(1)$; this structure corresponds to two or three CN -components arising from $K'=2$ and 3 (and possibly 1). A still better resolution (dispersion 57 Å./mm. and projected slit width 0.5 Å.) has been used by McKellar (6) on Comet Whipple 2; his spectrogram shows the resolution of the R branch-lines. The intense maximum near the (0, 0) head may be double, as in 1941 *c*: a first maximum is present at $P(11)$, λ 3880.3, the emission extending from $P(8)$ to $P(13)$, and a second maximum is observed at $P(15)$, λ 3881.7, the emission covering the interval $P(13)$ to $P(19)$. The other bands, especially the (0, 1) transition, reveal similarly complex structures (2).

The structures of the CN bands vary from comet to comet (2) and may even vary appreciably in a given comet (2, 7): this problem will be discussed extensively in section 4.

The so-called "tail bands" of CN belong to the same system, ${}^2\Sigma^+ \rightarrow {}^2\Sigma^+$, but arise from higher vibrational levels. They are absent in comets.

As for the red system of CN , (${}^2\Pi \rightarrow {}^2\Sigma$), the observational material is still rather scanty; yet it may be said definitely that in the spectral region $\lambda < 6600$ Å. the red system of CN , if present at all, is extremely weak. The only fairly good coincidence is that of a cometary line near λ 6333 with the strong (4, 1) band of the red system of CN .

Bands of CH .—The (0, 0) band of the $B^2\Sigma^- \rightarrow x^2\Pi$ system near λ 3900 is represented by a number of lines concentrated very close to the nucleus of the comet. All the lines observed in Comet 1940 *c* between λ 3886 and λ 3922 belong to CH ; they are listed in Table IV.

TABLE IV

(0, 0) Band of $B^2\Sigma^- \rightarrow x^2\Pi$ of CH in Comet 1940 *c*

Comet		Lab.	Designation		Comet		Lab.	Designation	
λ	Int.	λ	Branch	K^*	λ	Int.	λ	Branch	K^*
3886.6	o	86.4	Q_2	1	3897.2	1-2	97.5	P_1	2
3890.0	1-2n	89.1	Q_1	1			96.5	P_2	2
		89.8	Q_1	2	3902.6	1-2	02.6	P_1	3
		88.9	Q_2	2			02.0	P_2	3
		91.2	Q_1	3	3908.3	1-2	08.3	P_1	4
		90.5	Q_2	3			07.8	P_2	4
		91.1	P_2	1	3914.5	1	14.4	P_1	5
		90.1	$P_{Q_{12}}$	1			14.0	P_2	5
3893.1	1	92.9	P_1	1	3921.5	1-0	21.1	P_1	6
							20.7	P_2	6

* The J'' values are: $J'' = K + \frac{1}{2}$ for P_1, Q_1, R_1 ; $J'' = K - \frac{1}{2}$ for P_2, Q_2, R_2 .

The (0, 0) band of the $A^2\Delta \rightarrow x^2\Pi$ system is represented by a number of lines, some of which are very strong at small heliocentric distances. These lines are given in Table V. All the emissions observed in Comet 1940 *c* between λ 4280 and λ 4350 are unambiguously identified with CH . In particular, there is no trace of a line between λ 4304 and λ 4311, which might have been attributed to the strongest lines of the ${}^2\Delta \rightarrow {}^2\Pi$ (0, 0) transition of carbon deuteride.

The intensity distribution amongst the CH lines varies appreciably with heliocentric distance (see section 4).

Bands of C_2 .—The relative intensities among the Swan bands are very similar to the laboratory distribution at $T \simeq 3000^\circ$; this behaviour, which is related to the absence of a permanent electric dipole moment, will be discussed in section 4.

TABLE V

(o, o) Band of $A^3\Delta \rightarrow x^3\Pi$ of CH in Comet 1940 c

Comet		Laboratory			Comet		Laboratory		
λ	Int.	λ	Branch	K	λ	Int.	λ	Branch	K
4281	0-1	4280.1	R_1	5	4313.2	6n†	4312.2	Q_1	4
		4279.6	R_2	5			4312.2	Q_1	5
4285.7	1-0	4286.2	R_1	4			4311.6	Q_2	5
		4285.5	R_2	4			4311.3	Q_1	6
4291.7	1-2	4292.1	R_1	3	4329.3	1-2	4330.0	P_1	3
		4291.2	R_2	3			4328.9	P_2	3
4297.3	3n*	4298.0	R_1	2	4334.2	1-2	4334.8	P_1	4
		4296.6	R_2	2			4333.9	P_2	4
4300.2	2-3s	4300.3	R_2	1	4339.0	1-0	4339.3	P_1	5
4303.9	4s	4303.9	R_1	1			4338.7	P_2	5
4313.2	6n†	4314.2	Q_1	2	4344	0-1	4343.8	P_1	6
		4313.6	Q_1	3			4343.4	P_2	6
		4312.7	Q_2	3	4348	0-1	4348.2	P_1	7
		4313.0	Q_1	4			4347.7	P_2	7

* This line is not so sharp as the following one, λ 4300.† Extending from λ 4311 to λ 4315.

The Swan bands are the only transitions of C_2 in the observable region which involve the ground electronic level $A^3\Pi$. A further series of bands, often called the "high-pressure bands" or "Fowler's bands," was attributed until recently to another electronic transition involving the ground level $A^3\Pi$. G. Herzberg (8), however, has shown that they are simply Swan bands with $v'=6$. The selective excitation of the one vibrational level $v'=6$ would be due, according to Herzberg, to the fact that C_2 molecules in this state are formed by the recombination of two C atoms in a three-body collision, the heat of dissociation of C_2 being transformed into energy of excitation of C_2 . Such a process is hardly to be expected in a cometary head. A fairly strong band has often been measured at λ 5428, and sometimes attributed to one of "Fowler's bands," but this identification is not correct.

The five sequences $\Delta v = -2, -1, 0, +1, +2$ are observed in comets. In the $\Delta v = -1$ sequence the first four bands are very strong (successive intensities 9, 10, 8, 6) and the fifth at λ 5473 (4, 5) is extremely weak. Then come two more fairly strong bands, with maxima at λ 5445 (int. 4) and λ 5428 (int. 4). The latter coincides with the (5, 6) band of C_2 ("Fowler's band," see above), but is too strong to be due entirely to C_2 . No satisfactory identification can be found for λ 5445. There is no trace of an absorption band at λ 5427 or λ 5445 in carbon stars, where the first four C_2 bands of the $\Delta v = -1$ sequence are strong and the fifth absent.

Isotopes in Comets.—Numerous spectroscopic investigations of the carbon stars, especially by Stanford (9), have shown that C^{13} is present in the R and N stars, giving rise to absorption bands of $C^{12}C^{13}$, $C^{13}C^{13}$ and $C^{13}N^{14}$. The determination of the relative abundances of C^{13} and C^{12} in R and N atmospheres is rather difficult; but there seems to be good evidence that the abundance ratio of C^{13} and C^{12} is sometimes higher than on the Earth, and may be different in different carbon stars. In view of the fact that the strong emission bands of the comets are the same as the intense absorption bands of the carbon stars, Bobrovnikoff (10) examined the Lick Observatory cometary spectra for evidence of bands due to $C^{12}C^{13}$. He observed a faint band at λ 4744 (11) on several spectrograms of Comet Brooks and Comet Halley. New measurements of these spectrograms by the author are in excellent agreement with Bobrovnikoff's results, and there seems to be little doubt that the band should actually be attributed to $C^{12}C^{13}$. On the other hand, the spectrograms of Comet 1940 c taken at the McDonald Observatory fail to reveal any trace of λ 4744, despite the fact that the ordinary Swan bands are

sometimes strongly over-exposed. Thus it seems difficult to escape the conclusion that the relative abundance of C^{13} and C^{12} may be different in various comets. In any case, as already stated by Bobrovnikoff, no comet has been observed which shows isotopic bands of intensities comparable to those in the N stars. In this connection it should be pointed out that the relative intensities of $\lambda 4737 C^{12} C^{12}$ and $\lambda 4744 C^{12} C^{13}$, measured by Jenkins and A. S. King (12) in meteoritic graphic and in ordinary Acheson graphite, failed to reveal any difference between the two samples.

Besides $\lambda 4744$, Bobrovnikoff also observed a faint band at $\lambda 4751$ which is probably the (1, 0) band of $C^{13} C^{13}$. Moreover, Brooks's comet revealed also very faint bands measured by Wright (13) at $\lambda 4723$ and $\lambda 4706$. It is extremely probable that these two features are the (2, 1) and (3, 2) bands of $C^{12} C^{13}$. They cannot be accounted for as peculiar band maxima due to the distortion of the rotational intensity distribution in the $C^{12} C^{12}$ bands. The evidence for the presence of C^{13} in comets may thus be summarized as follows:—

- $\lambda 4753$: (1, 0) transition of $C^{13} C^{13}$.
- $\lambda 4745$: (1, 0) transition of $C^{12} C^{13}$.
- $\lambda 4723$: (2, 1) transition of $C^{12} C^{13}$.
- $\lambda 4706$: (3, 2) transition of $C^{12} C^{13}$.

The bands of $C^{12} C^{13}$ are hazy, whereas the $C^{12} C^{12}$ bands have sharp edges: this difference of profile will be explained in section 4.

No trace of the (0, 1) band of $C^{13} N^{14}$ has ever been detected (head at $\lambda 4208.4$, against $\lambda 4216.0$ for $C^{12} N^{14}$). But this may be simply because the (0, 1) band of CN is usually not strong, and also because the abundance ratio of $C^{13} N^{14}$ to $C^{12} N^{14}$ is half that of $C^{13} C^{12}$ to $C^{12} C^{12}$.

A systematic search for the isotopes of other elements, especially for deuterium, failed to reveal any isotopic band on the Lick or on the McDonald cometary spectrograms. This result indicates that no spectroscopically observed comet has presented abnormally high isotopic abundances compared to the Earth.

Lines of CH⁺.—Among the cometary features which were still unidentified two years ago, there is a group of three lines at $\lambda\lambda 4231, 4238$ and 4254 , appearing in the wavelength range between the $\Delta v = -1$ sequence of CN and the strong CH lines. This group deserves special attention because it extends, at least partly, into the tail. It has been measured in various comets, especially in Comet Brooks by Wright (13), in Comet Morehouse by de la Baume Pluvinel and Baldet (14) and in Comet Cunningham by the author (15). The measurements are given in Table VI, which contains also the wavelengths of unidentified features listed by Baldet (16).

TABLE VI

Group of Cometary Lines near $\lambda 4240$

Comet Brooks *		Comet Morehouse		Comet Cunningham †		Unidentified Nuclear Lines	
λ	Int.	λ	Int.	λ	Int.	λ	Int.
4230	0	4231.1	1n ‡	4230	1
4238.5	0	4236	3 §	4240.4	1-2n	4238	1
4254.5	0	4250	2	4254.3	1n	4255.8	2
...	...	4257	10

* Long lines, present in head and tail.

† Especially conspicuous on the spectrograms of 1940 December 27, 28 and 31 (heliocentric distances 0.65, 0.63, and 0.58); the lines extend farther from the nucleus than the CH bands. On the quartz spectrogram of 1940 December 28, showing the tail spectrum, the lines extend far out into the tail.

‡ Possibly double at $\lambda 4229.1$ (int. 1) and $\lambda 4231.8$ (int. 1).

§ Present in head and part of tail.

|| Present in head and tail; main contributor, CO⁺.

There is little doubt that the lines measured in Comet Morehouse at λ 4250 and λ 4257 are mostly due to a band of ${}^2\Pi \rightarrow {}^2\Sigma$ of CO^+ (comet-tail system), and this will apply to any line measured in the tail near λ 4254. But this is not the case in the head, when the other CO^+ bands of similar intensity are absent. In the head, the line λ 4238 cannot be attributed to the (1, 2) transition of N_2^+ (${}^2\Sigma \rightarrow {}^2\Sigma$) when the (0, 0) band of N_2^+ at λ 3914 is not observed. There is a strong transition of SiN at λ 4239 (system ${}^2\Sigma \rightarrow {}^2\Sigma$, band 4, 4), but this cannot contribute appreciably to the observed feature, since the stronger band at λ 4204 is not observed.

The only satisfactory identification that suggests itself is to attribute the three lines to the (0, 0) band of CH^+ (system ${}^1\Pi \rightarrow {}^1\Sigma$) (17). In this case we might also expect a faint (1, 0) band to be present, since in interstellar absorption the CH^+ molecules reveal their presence by the $R(o)$ lines of the three transitions (0, 0), (1, 0) and (2, 0) (17). The unidentified cometary lines that have been observed in the region between λ 3953 and λ 3975 are listed in Table VII. We may expect that some of these lines are due to the CH_2 molecules giving rise to the " λ 4050 group." The (0, 0) band of the Baldet-Johnson system of $CO^+(B^2\Sigma \rightarrow A^2\Pi)$, the lower level $A^2\Pi$ being the upper state of the comet-tail bands) does not contribute, since the other transitions (1, 0) and (0, 1) of similar intensity are absent (18).

Thus it is suggested that the features near λ 4240 and λ 3960 are due, at least partly, to CH^+ , according to the identifications listed in Table VIII, where the cometary wavelengths given in the first column are average values estimated from Tables VI and VII. The CH^+ molecules are present in the head and in part of the tail.

TABLE VII
Group of Cometary Lines near λ 3960

Comet Brooks *		Comet Cunningham †		Unidentified Nuclear Features ‡	
λ	Int.	λ	Int.	λ	Int.
...	...	3954.0	1
		3960.2	1-2
3963	0	3963.5	1-2	3962.5	0
...	3968.4	2
3974	0	3972.7	2	3974.8	0

* Wright, *Lick Obs. Bull.*, 7, 8, 1912.

† Swings, Elvey, and Babcock, *Ap. J.*, 94, 342, 1941. The lines $\lambda\lambda$ 3954, 3963 and 3973 were enhanced, together with $\lambda\lambda$ 4231, 4238 and 4254, on the spectrograms of 1940 December 27 and 31.

‡ Baldet, *Ann. obs. astr. phys.*, Paris, 7, 58, 1926.

The observed lines of CH^+ arise mainly from the rotational levels $J' = 1$ and 2. This "low temperature distribution" is similar to that observed for CH , NH , OH and CN .

The effective slit width for the spectrograms of Comet Cunningham is 1.9 A. near λ 4240; thus the separation of the $Q(1)$ and $Q(2)$ lines of the (0, 0) band is impossible, while $R(0)$ and $R(1)$ may be resolved. The region between λ 3940 and λ 4000 is complex, whereas that around λ 4240 contains no lines other than $\lambda\lambda$ 4231, 4238 and 4254. The evidence in favour of CH^+ from the (0, 0) band is, therefore, more convincing than that from the (1, 0) transition. No line was observed in the region of the (2, 0) band.

On the whole, the evidence in favour of CH^+ is satisfactory. Like CO^+ and N_2^+ , CH^+ molecules are present in the head as well as in the tail, but the extension of CH^+ into the tail is shorter than that of CO^+ and N_2^+ .

The CH_2 Band.—Until quite recently a group of strong lines near λ 4050 remained the most puzzling group of unidentified cometary features. Many elaborate discussions have been published on this group, which has been variously attributed to CH (Raffety

TABLE VIII
CH⁺ Lines in Cometary Spectra

Comets		Laboratory		Comets		Laboratory	
λ	Int.	λ	Notation	λ	Int.	λ	Notation
4231 *	I	4232.54	R(0)	3954	I	3955.49	R(1) + R(4)
		4229.34	R(1)			3954.37	R(2) + R(3)
4238.5	I-2	4237.56	Q(1)	3963	I-2	3962.07	Q(1)
		4239.37	Q(2)			3964.26	Q(2)
4254.4	I	4254.39	P(3)	3972	I-2	3970.82	P(2)

* The two components measured on one spectrogram at λ 4229.1 (int. 1) and λ 4231.8 (int. 1) would be the R(1) and R(0) lines, respectively.

band), C₂ (Deslandres-d'Azambuja system ¹Π → ¹Π), CN (tail bands), NaH, etc. . . . None of these attempts has given a satisfactory identification.

The "λ 4050 group" consists of a strong, fairly sharp line at λ 4051.5, accompanied by weaker lines on either side, as schematized in fig. 2. It is observed in the central parts of the coma, more or less concentrated near the nucleus.

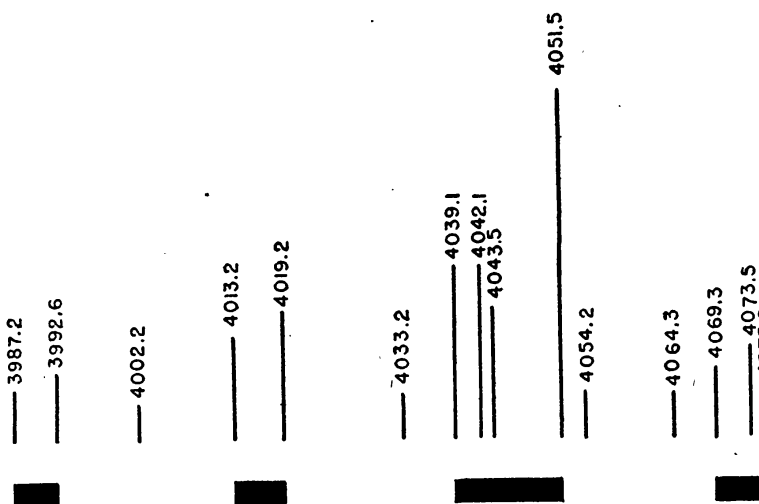


FIG. 2.—Diagram of the λ 4050 group.

When observed with a dispersion of 55 Å./mm. and an effective slit width of 0.8 Å., 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 λ 4051. This behaviour is illustrated in Table IX. In Comet Cunningham, whose spectrum 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 λ 4050 group was extremely weak, while CN and C₂ were very intense; but CH was also absent.

Certain general conclusions may be obtained regarding the identification of the λ 4050 group.

Let us first consider the case of a diatomic emitter. In order to give sharp lines with a dispersion of 55 Å./mm., the diatomic molecule must be a hydride. All the diatomic

TABLE IX
Relative Behaviour 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

hydrides (neutral and singly ionized) of the light elements are known, except NH^+ . In any case, however, the emitter cannot be a neutral hydride, otherwise it would have been found in late-type stars. If the emitter is NH^+ , which is iso-electronic 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 and $\lambda 4039.1$ 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 origin is uncertain. The B_0'' value obtained turns out to be 13 or 14 cm^{-1} , as compared with $B_0''(NH) = 16.33 \text{ cm}^{-1}$.

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 (19). The spectrum of NH^+ would also be expected a little more to the red (20). 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 should 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 (21). In this direction, Dr. Herzberg has recently suggested (22) that the group may be a \perp band of a nearly symmetric top molecule, the observed series of bands (tentatively indicated in fig. 2) corresponding to the sub-bands. The corresponding molecule can only be CH_2 or NH_2^+ , of which CH_2 is the more likely. Actually Dr. Mulliken had predicted last year the existence of an electronic transition of CH_2 in the region 4000-4500 A. (23).

From the astronomical point of view, CH_2 is an excellent suggestion, because we should then understand easily why the intensity ratio of $\lambda 4051$ to $\lambda 4313$ (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.

From these observations, we could conclude in 1942 June 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. During the summer of 1942 Herzberg succeeded in reproducing

the λ 4050 group in the laboratory, an achievement vainly searched for before. Herzberg's announcement (24) is reproduced here:

"On the basis of the assumption that the λ 4050 group is due to CH_2 , it was considered likely that it would occur in an electrodeless discharge through methane if the gas was rapidly streaming through. It was found that with moderate pumping speed a continuous discharge through CH_4 gave only the H_2 , H and, comparatively weakly, the CH spectrum. However, it was noted that immediately after turning on the discharge the colour was distinctly different from the one established later (bluish white, as compared to the pinkish-white characteristic of hydrogen). This observation suggested that, in spite of the continuous stream of CH_4 , the gas was completely decomposed in the discharge except in the first fraction of a second, and the occurrence of CH_2 in the first flash appeared more likely than afterward. The spectrum of an interrupted discharge through streaming CH_4 , which was on only for about $1/4$ second every 4 seconds, did, indeed, show a new group of bands which proved to be identical with the λ 4050 group observed in comets. With higher pumping speeds, using wider and shorter connecting tubes, it was possible to obtain the λ 4050 group even without interrupting the discharge, although it was then more strongly overlapped by the H_2 spectrum.

"In the upper part of Plate 5 the spectrum of an interrupted discharge through streaming CH_4 (with iron-arc comparison spectrum) is reproduced. It has been enlarged to the same scale as a spectrum of Comet 1940 *c*, which is given in the lower part of the plate, also with *Fe* comparison spectrum. From a comparison of the two spectra, the identity of the λ 4050 group occurring in comets with the group observed in the laboratory seems to be definitely established, particularly if it is remembered that (1) there are a few H_2 and CH lines overlapping the laboratory spectrum, (2) small differences may be expected on account of the different mechanism of excitation, and (3) this group is the only new feature of the laboratory spectrum, which otherwise consists only of H , H_2 and CH lines and bands in the whole visible and ultraviolet regions.

"The freedom from impurities shown by the spectrum makes it practically certain that the λ 4050 group is due to a molecule containing carbon and hydrogen. The method of excitation suggests a molecule intermediate between CH_4 and CH . Thus the previous conclusion (22) that the emitter is CH_2 , which was based on the structure of the spectrum, is strongly supported, although, from the conditions of excitation alone, CH_3 and CH_4 cannot be excluded. By an investigation, now under way, of the fine structure of these bands, a definite decision will be possible."

Thus was identified the first polyatomic molecule of comets. Herzberg is now engaged in the analysis of his laboratory spectrograms of the " λ 4050 group" (25).

3. Cometary Emissions in the Visual Region

Spectra of comets have been observed toward the long wave-lengths up to λ 6650 approximately; some observations have been made beyond λ 6650, but they are only of a preliminary character and do not provide reliable identifications. The yellow and near red regions are comparatively poorly known, the reason being that modern grating spectrographs have hardly been used to investigate comets. Yet, despite the low dispersion always used in the visual region, it seems desirable at the present time to collect the data available in the region $\lambda > 4800$ A. The wave-lengths of the emission lines to the red of λ 4800 are given in Table X, from which have been excluded the well-identified C_2 and CN bands (26). Some of the faint lines listed in the table may be spurious, especially those which are concentrated near the cometary nucleus where the intensity of the reflected solar spectrum is strong.

The strongest unidentified line is λ 6299 which behaves very much like the CH_2 band. At large heliocentric distance, λ 6299 stands out conspicuously; for example, in Comet 1942 *f* ($r = 1.36$), there is hardly any trace of CH , the NH and C_2 bands are

TABLE X
Cometary Emissions in the Spectral Region $\lambda > 4800$

Brooks (1)	Peltier (2)	Finsler (3)	Cunningham (4)						Cunningham (5) $r = 0.5$	Whipple 2 (6)	Whipple 2 (6)	Nuclear Features (7)	Adopted Wave-length	Suggested Identification
			$r = 0.85$	0.71	0.69	0.65	0.58	0.52						
4837.8 (o)			67.6 (1s) (8)	38.3 (2)	39.7 (1n)	38.8 (1+)	39.6 (2n)	40.0 (1+)	36.5 (on)		40.4 (3)	4838.9	NH ₂	
			77.0 (o+?)	76.0 (1f)	75.2 (o+)	84.9 (1)	78.8 (1n)	69.2 (1-)			66.6	4868.2		
4925.5 (o+)	25.6 (..)		23.8 (2)	25.2 (2)	26.2 (1+)(8)	25.8 (2)	25.6 (2)	25.4 (2)			74	4876.0		
			36.0 (1-)	38.0 (1)	38.0 (1)	53.3 (1)	51.6 (1)				70.5	4883		
			54.9 (o+)	52.9 (o+)	54.0 (1-)						28.5 (3)	4925.7		
			62.9 (o+)	71.7 (o+)							48	4937.0		
			70.4 (o+)								62.5	4953.3		
			06.0 (1-)								71.1	4962.7		
5178 (o)			85.5 (2)	43.3 (1-)(10)	43.2 (1+)(10)	43.2 (1+)(10)	42.7 (1+)(10)				08	5007.0		
				59.0 (1-)(10)							78 (o)	5186.5		
				83.5 (1-)(10)								5243.1	NH ₂	
			16.4 (1)	18.8 (1+)	19.5 (1+)(10)	18.5 (2+)	19.4 (2)					5283.5		
			26.0 (1-)	32.9 (1)	33.6 (1+)(10)	36.2 (2)	36.2 (2)					5318.5		
			36.8 (1-)	52.7 (1)	57.9 (1+)	52.8 (2)	52.8 (2)					5326.0		
			57.0 (1n)	83.2 (1+)	84.0 (2f)(10)							5336.5		
			92.0 (1)									5355.3		
5418.5 (o)			26.5 (4)	28.0 (4)	29.8 (3) (8)	28.3 (4)	28.8 (3)				18.5 (o)	5386.4		
5428.3 (1-)		29 (2n)	43.7 (4)	43.2 (4)	44.0 (3) (8)	47.3 (4)	47.0 (2)					5418.3		
5692.5 (o)		43 (2n)	79.1 (1)	99.0 (2+)	89.8 (o+)	99.9 (3n)	01.3 (3)					5428.0		
5705 (1n)	97 (..)	10 (1n)	01.0 (2+)	04.5 (1n+)(11)	04.5 (1n+)(11)	18.9 (1)	19.4 (1+)	44.7 (1)				5445.0		
			35.2 (2)	31.0 (2)	31.6 (2)	31.3 (2)	38.7 (1n+)	95.6 (2n)			925 (o)	5689.0		
5732 (o)		37 (1s)	39.5 (1+)	38.9 (1+)	38.9 (1+)	41.3 (1+)	38.7 (1n+)	28.9 (1n+)			05 (1n)	5702.7		
		47 (1s)	53.4 (1)	51.4 (1)	51.4 (1)	54.7 (1)						5719.2		
5779 (1-)	14 (..)		01.3 (1-)	05.8 (o+)	05.8 (o+)						32 (o)	5731.5		
			92 (1f)	93 (1n?)	93 (1n?)	92.9 (2n)	93.2 (1n)	Na			32 (1s)	5740.4		
5977 (1-)	71 (..)	81 (2n)	78.0 (4)	78.1 (4)	75.0 (4)	78.8 (5)	76.3 (4)	76.1 (4)			42 (1-)	5740.4		
5994 (1-)		98 (1n)	97.4 (3)	96.5 (3)	92.8 (2)	96.2 (1+)	94.1 (2)	95.0 (2)			56 (o+)	5754.1		
											89 (o)	5768		
											79 (1-)	5789		
												5805.0		
												5892.8		
												5976.8		
												5996.0		

6020.5 (o)	15 (1n)	20.2 (2)	18.1 (2)	21.7 (2)	21.8 (1+)	(18)	17.6 (2)(18)		21 (o+)	20 (oon)	18 (1-)	20.5 (o)	NH ₂ NH ₃ C ₂ +NH ₂ NH ₂
45 (...)	34.9 (1n+)	41.0 (2-)	41.0 (2-)	57.0 (1?)	(16)	(18)	34.8 (1)	51 (1n)		50 (on)			6019.4 6036.9 6053.5 6085.3
79 (...)	54.4 (1)	79.8 (1+)	79.8 (1+)	96.2 (2+)	(16)	(17)	55.3 (1)	98 (1)	99 (o)	97 (1nm)	96 (1+)		6098.0 6110.2
02 (...)	00 (1n)	96.7 (2+)	99.0 (3)	99.6 (2)	(16)	(17)	90.8 (2)	17 (4)		47 (onm)	10 (o+)		6120.9 6148.6
	18 (on)	13.7 (4)	19.5 (2)	20.6 (1?)	(16)	(17)	02.4 (2)						6170.6 6200.2
			64.4 (1-)	73.4 (o+)		50.1 (o+)	17.8 (2)						6244.1 6279
						74.1 (1)							6298.7 6320
6300 (1)	06 (3)	98.0 (5)	97.2 (5)	99.3 (5)	98.7 (6)	96.0 (2)	96.8 (5)	[OI]	00 (2)	97 (3n)	00 (5) ⁽¹⁰⁾	00 (5)	NH ₂ +CN NH ₂
	38 (2)	30.4 (1+)			29.3 (1)			37.6 (1)	36 (o)	36 (1)	20 (o+)		6333.4 6345.8
	67 (1)	62.3 (1)						[OI]		45.6 (1-)	33 (2)		6363.4 6386.2
	30 (...)							13.7 (1)		86.2 (on)	62 (1)		6407 6546
6578 (o)	83 (1)								81 (o)	46 (oos)	00 (o+)		NH ₂ ? NH ₂
6598 (1)	24 (2)								19 (1+)		79 (o+)	78 (o)	6580 6598
6619 (1)	46 (1)								68 (o-)	25 (oos)	20 (3)	10 (1)	6621 6642
									85 (o)	38.4 (on)	75 (o+)		6668 6685

- (1) W. H. Wright, *Lick. Obs. Bull.*, **7**, 8, 1912.
(2) Baae and Minkowski, *Pub. A.S.P.*, **48**, 277, 1936.
(3) R. L. Minkowski, *Pub. A.S.P.*, **49**, 276, 1937.
(4) Unpublished measurements by the author.
(5) A. McKellar, private communication.
(6) R. L. Minkowski, private communication.
(7) F. Baldet, *Ann. Obs. Astr. Phys.*, Paris, **7**, 1926.
(8) Long line.
(9) Probably double at λ 4924.3- λ 4928.5.
(10) Nuclear.
(11) Possibly double at λ 5700.7- λ 5705.8.

- (12) This nebulous feature is not the D-line of Na which became definitely present as a sharp line for $r=0.52$.
(13) Broad band with structure, from λ 6017 to λ 6058.
(14) From λ 6021 a band extends to λ 6062 with a maximum at λ 6050.
(15) Broad band, intensity 1+, from λ 6032 to λ 6059.
(16) Band from λ 6095 to λ 6124 with probable maxima at $\lambda\lambda$ 6100.4 (2⁺), 6111.0 (2) and 6121.6 (2⁺).
(17) Band from λ 6091 to λ 6122.
(18) Not due to C₂ (o, 2) only.
(19) Extending from λ 6296 to λ 6303. Measured by Swings and Struve in Comet Whipple 2: $\lambda\lambda$ 6299.0 (5), 6330.5 (1), 6345.6 (1-), 6366.3 (1), 6380.4 (o⁺).
(20) Identification not satisfactory, since the cometary line is long.

weak, but $\lambda 6299$ and $\lambda 4051$ CH_2 are both quite strong. There is no strong absorption band in late-type stars at $\lambda 6299$. A number of features to the blue and to the red of $\lambda 6299$ behave similarly with heliocentric distance, but additional observations are desirable on this point. Provisionally we suggest calling this group of emissions the " $\lambda 6300$ group," and there is every reason to believe that it belongs to a polyatomic molecule.

The only identification which suggests itself for the " $\lambda 6300$ group" is the α band of ammonia. The α -band appears easily in many types of flames (27) and discharges (28). Its structure is very complex; of more than 3000 lines observed with high dispersion, some 300 have been measured by Rimmer. Excellent reproductions of the low-dispersion spectrograms of the hydrogen-nitrous oxide and methane-nitrous oxide flames, in which the α -band is present, have been published by Gaydon (27). In the hydrogen-nitrous oxide flame, two intensity maxima at $\lambda 6300$ and $\lambda 6330$ are very outstanding, but they vary somewhat in intensity from plate to plate. In the methane-nitrous oxide flame, the features at $\lambda 6300$ and $\lambda 6330$ are not outstanding. In Eder and Valenta's reproduction of the ammonia-oxygen flame, the features at $\lambda 6300$ and $\lambda 6330$ are also conspicuous. From Gaydon's observations it would appear that $\lambda 6300$ and $\lambda 6330$ are "not of the same origin as the rest of the α -band, or that for some reason they are particularly sensitive to changes in the temperature of the flame." In 1927 Hulthén and Nakamura (29) had already suggested that the α -group "is emitted by the excited NH_3 or NH_2 molecules, or a mixture of both, as one can distinguish with some degree of certainty two different systems in α ." Whatever doubt there remains as to the molecules which actually give rise to the α -band, it is certain that they must be nitrogen-hydrogen polyatomic combinations (probably not ionized), NH_2 playing the dominant rôle.

The electronic structure of NH_2 has been considered by R. S. Mulliken (30), who has kindly provided a number of additional data. The level diagram (fig. 3) indicates

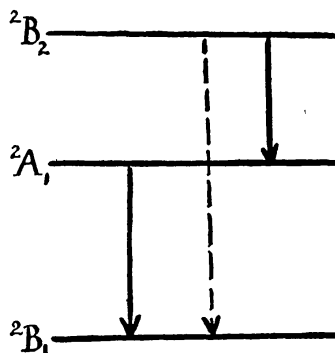


FIG. 3.—Level diagram of the NH_2 molecule (after R. S. Mulliken).

the nature of the expected transitions on the assumption that the apex angle is fairly wide, as may be inferred by analogy with Herzberg's interpretation of the cometary CH_2 group (31). The diagram suggests that there might be NH_2 spectra observable in the visible region. It seems hardly likely that the interval between 2B_1 and 2B_2 could be more than four volts. The position of 2A_1 would depend a good deal upon the apex angle; for a smaller apex angle, such as that for H_2O , the levels 2A_1 and 2B_2 might be close together or even reversed in position.

From all of this it appears that there may be either one or two moderately intense spectra of NH_2 in the visible region. It is also possible that the molecule has an almost metastable level if the highest level shown in fig. 3 is actually the middle one; however, this is improbable (32).

In the absence of an analysis of the α -band, it is impossible to predict in detail the

structure of the emission by cometary NH_2 molecules excited by solar radiation. Hence there remains only the crude method of comparing the wave-lengths of the intensity maxima in the laboratory source and in the comet, it being well understood that slight differences in wave-length and larger ones in intensity may be expected. Moreover, it should be pointed out that the NH bands are strong in comets, and that the NH molecules must result from the photo-dissociation of chemically stable parent molecules (probably ammonia) liberated by the solid constituents of the comet. Hence the presence of NH_2 bands is likely, since it is known (33) that the photo-chemical decomposition of ammonia takes place almost exclusively according to the reaction



It seems very probable that the cometary features at λ 6299 and λ 6333 are identical with the strong lines of the α -band. From wave-length and intensity comparisons it is also hard to escape the conclusion that an important part of the emissions, from the nuclear region, of the λ 6300 group—besides λ 6299 and λ 6333—actually belongs to the α -band of ammonia (see Table X). The author has just learned that A. McKellar and R. Minkowski also identified the NH_2 bands independently; see Swings, McKellar and Minkowski, *Ap. J.*, in press.

As to the other unidentified features the following remarks may be made:—

(a) The cometary line λ 4839 is very near to the strong Vegard-Kaplan band of N_2 at λ 4837.1. But the identification is very doubtful, since other Vegard-Kaplan bands of similar intensity in the night sky are absent.

(b) The features at $\lambda\lambda$ 4868, 4937 and 4971 are close to the wave-lengths of unidentified absorption bands found by Sanford (34) and Shane (35) in carbon stars. In carbon stars λ 4976 has been tentatively attributed (36) to the convergence of the $\Delta v = 0$ sequence of C_2 .

(c) The three cometary emissions at $\lambda\lambda$ 5318, 5326, 5336 may be identical with a new system of nitrogen recently found by Gaydon (37).

(d) The (4, 1) band of the red system of CN may contribute to the cometary feature at λ 6333.

(e) The cometary emission at λ 5996 is not due to NO^+ . A strong band with origin at λ 5999 has been attributed to NO^+ (38), but by comparison with CO it is certain that this band cannot be a resonance transition of NO^+ . By analogy with CO , we should expect the absorption required to reach the higher electronic level of the λ 5999 band of NO^+ to be situated in the far ultraviolet; hence excitation by solar radiation would be very inefficient.

(f) The cometary emissions at λ 6299 and λ 6364 are occasionally blended with the [OI] lines of the night sky.

4. The Excitation Mechanism and the Rotational Structure of the Cometary Bands

It has usually been assumed that the molecular bands, and also the Na lines, are emitted in a fluorescence process excited by solar radiation (39). This suggestion was put forward by Schwarzschild and Kron in 1911 (40), and developed theoretically by Zanstra (41) in 1928, and by Wurm (42) in 1934. 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. Wurm also concluded, from the estimated intensity of the C_2 bands, that the pressure in the nucleus is probably less than 10^{-10} mm., and much less than this in the head and tail. This indicates that collisional effects must be unimportant in cometary atmospheres.

A more direct test of the fluorescence hypothesis is provided by Öhman's measurements of polarization (43) in Comet Jurlof, and especially in the spectra of Comet Cunningham and Comet Paraskevopoulos. The theoretical basis is the following (44):

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 transitions such as $\Sigma \rightarrow \Pi$, . . . (involving a change in Λ) the polarization should be 19 per cent. "If the values obtained for comets should be found to be lower than the values given above, it would show the presence of an additional unpolarized excitation of molecules, such as excitation by electron impacts, collisions, etc., the amount of which could be easily estimated from the degree of polarization found" (Mrozowski, *loc. cit.*).

Such measurements of the polarization of cometary bands are difficult to perform, yet those made by Öhman have met with a great deal of success. For the C_2 and CN bands of Comet Cunningham, Öhman finds a polarization of about 10 per cent., which is approximately that to be expected for a pure fluorescence excitation. In Comet Parakevopoulos Öhman finds a much higher polarization, about 24 per cent.; this Öhman attributes to the fact that most of the light of this latter comet (which had a strong solar spectrum and only faint bands) is due to diffuse reflection, diffraction or scattering of solar light by cometary particles.

Öhman's success is promising, and renewed attempts should be made with a view to increasing considerably the accuracy of the measurements. However, since such very accurate determinations are very delicate, it is desirable to search for a more direct, spectroscopic test of the fluorescence hypothesis.

Such a test was provided by the author (45) in 1941 and was the object of important microphotometric work by McKellar (46) in 1942 and 1943. The question is to decide whether the molecules are brought into the excited state by absorption of radiation only, or whether dissociation or collisional processes could provide the excitation energy. For example, does the CN emission result from a photo-dissociation such as $C_2N_2 + h\nu \rightarrow CN_{exc} + CN$, or simply from a pure resonance excitation $CN + h\nu \rightarrow CN_{exc}$?

There is a possibility of deciding between these two mechanisms on the basis of the intensity distribution among the rotational lines of the individual bands. It was shown in sections 1 and 2 that except for the Swan bands of 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, this being especially characteristic in the case of CN . In all the cometary molecules which have a permanent electric dipole—and therefore excluding $C^{12}C^{12}$ —only the lines arising from the low rotational levels are observed:

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

But the intensity distributions among these lines of low rotational quantum number deviate considerably from the smooth distributions in equilibrium at a low temperature. For example, in the excited level $v' = 0$ of CN , the rotational states $K' = 2$ and 3 (always), 8, 11 and 15 (often) are favoured as compared with $K' = 5$, which is underpopulated (47). The rotational intensity distribution is not quite the same in all comets, but all manifest a number of favoured excited rotational levels.

If we assume an excitation in comets resulting purely from one or several photo-dissociations or from electron impacts, we must admit that the selective favouring of certain rotational levels is due to these mechanisms. No laboratory or theoretical data favour such an effect, and it would be impossible to explain in this way the variations of the observed CN structures with heliocentric distance or from comet to comet.

Let us now 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:—

$$N'_{K'} \propto N''_{K'+1} \cdot P_P^{abs} \cdot I_P + N''_{K'-1} \cdot P_R^{abs} \cdot I_R \quad (3)$$

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^{abs} and p_R^{abs} , the transition probabilities of the absorption line $sP(K' + 1)$ and $R(K' - 1)$ and
 I_P and I_R are the intensities of solar radiation for the wave-lengths 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 ± 0.25 A.).

Whatever the distribution $N''_{K''}$ may be (the simplest case is a continuous function of K'' with only one maximum), $N''_{K''}$ will depend on the spectral distribution of the solar radiation. The important effect of the Fraunhofer lines appears strikingly when one plots the wave-lengths of the P and R lines on a map or a photometric tracing of the solar spectrum. The deep minima in the solar spectrum in the region of $P(6)$ and

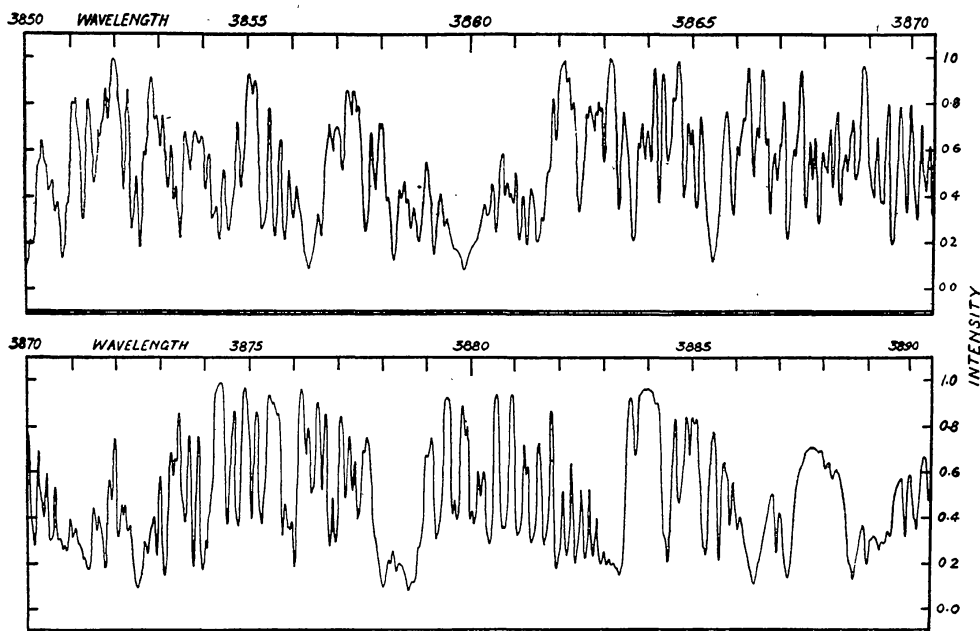


FIG. 3A.—Contour of the solar spectrum near the λ 3883 band.

$P(7)$, and between $R(2)$ and $R(7)$ are undoubtedly the cause of the very low intensity of the P and R lines corresponding to $3 < K' < 8$. Whatever the radial velocity may be, $P(6)$ and $P(7)$ will always fall in a deep minimum of the solar spectrum, caused mainly by λ 3878.02 (FeI , lab. int. 400, \odot 8) and λ 3878.57 (FeI , lab. int. 300, \odot 7) (fig. 3A). Also $P(5)$ usually falls in a solar spectral region fainter than that near $P(4)$. Another minimum in solar intensity occurs between $P(9)$ and $P(12)$. On the whole, it is possible to explain the observed structures in cometary spectra by assuming that the intensity maxima and minima result from solar excitation influenced by the Fraunhofer lines.

The effect of the radial velocity of the comet with respect to the Sun should be pointed out. Whereas no probable radial velocity could prevent $P(6)$ and $P(7)$ from falling in a weak region, certain relative intensities may be very sensitive to a change in radial velocity which could bring the cometary absorption line inside or outside a strong Fraunhofer line. These considerations, when applied to various comets having different radial velocities with respect to the Sun, but with similar heliocentric distances, have given a satisfactory interpretation of the observed CN structures. These same considerations may, of course, be equally well applied to one comet at different heliocentric

distances. Similar considerations when applied to the other molecules, *CH*, *NH* and *OH* give a satisfactory qualitative explanation of band structures.

Quantitative Test of the Fluorescence Theory in the case of the CN Bands.—All the preceding considerations are of a qualitative character, and although they provide very strong evidence in favour of a pure fluorescence excitation, a quantitative microphotometric discussion was highly desirable. Such an investigation was also likely to provide interesting data on the rotational distribution of the molecules in the ground electronic state. This has been performed by McKellar for Comets 1939 *d* (Jurlof) and 1940 *c* (Cunningham), using slit spectrograms taken at the Dominion Astrophysical Observatory in Victoria, B.C. Profiles were obtained for the λ 3883 (0, 0) band of *CN*, the λ 4315 band of *CH*, and the $\Delta v = +1$ sequence of *C*₂. Fig. 1 gives the *CN* band profile of Comet 1940 *c* for $r = 0.54$ (mean of three spectrograms at $r = 0.56, 0.54$ and 0.52) and for $r = 0.92$ (mean of three exposures at $r = 0.97, 0.93$ and 0.87). There is a decided difference in the profile of the *P* branch for the two heliocentric distances, which is most directly and readily interpreted as an increase in “rotational temperature” of the *CN* molecules as r decreases. This effect had been found previously (48), but is now more clearly defined. As mentioned by McKellar, it explains the striking and long unexplained difference between the *CN* bands in the spectra of Comet Zlatinsky (1914 *b*) at $r = 0.67$ and Comet Mellish (1915 *a*) at $r = 1.52$ (49).

To calculate the profiles of the *CN* bands on the assumption of a pure fluorescence mechanism, McKellar adopts a Boltzmann type of distribution for the rotational levels of the ground state. The “rotational temperatures” were chosen to give the best agreement in wave-length between the observed main maximum of the *P* branch and the corresponding maximum of the computed intensity curve. In applying formula (3) the intensities were taken from the Utrecht Photometric Atlas of the Solar Spectrum (50), with due correction for radial velocity shift (fig. 3A). The computed relative intensities of the emission lines were then plotted as rectangles of height proportional to the calculated intensity and width equal to the projected spectrographic slit width (51). A few obvious transformations of the calculated diagrams were applied, in order to make them as nearly comparable as possible with actual profiles. The calculated *R* branch remains still too intense, compared with the *P* branch, but this does not affect the main conclusions.

The results of the calculations are shown in figs. 4 and 5 for Comet 1940 *c*. It is apparent at once that virtually every intensity maximum has its corresponding counterpart in the calculated profile. Had the effect of the contour of the solar spectrum been neglected, then the calculated profiles would have been smooth, with no subordinate maxima.

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

The influence of the radial velocity, already considered by the author in 1941, has been studied more in detail by McKellar, who showed that the considerable shift of the *CN* maximum in Comet 1939 *d* ($r = 0.59$) relative to Comet 1940 *c* ($r = 0.54$) is due to the difference in radial velocities. The radial velocity of Comet 1940 *c* with respect to the Sun was about 33 km./sec. of approach, while for Comet 1939 *d* it was 16 km./sec. of recession. In Comet 1940 *c* the whole solar spectrum was effectively shifted some 0.45 Å. to the violet; therefore the strong region of the solar spectrum from λ 3883.4 to λ 3883.9 (see fig. 3A) was effectively at λ 3883.0 to λ 3883.5 and so helped greatly to increase the populations of the levels from $K' = 21$ upwards. However, for Comet 1939 *d*, the solar spectrum was effectively shifted some 0.21 Å. to the red, which caused an underpopulation of the levels from $K' = 20$ upwards.

It is also certain that slight changes in radial velocity may affect appreciably the intensity of the cometary *CN* emission because of the shift of the solar spectrum: this point deserves further study.

Other Molecules.—The author's qualitative discussion of the CH , NH , OH and CH^+ bands, and McKellar's quantitative study of the $\lambda 4315$ CH band show that the fluorescence mechanism is also responsible for the excitation of these other molecules,

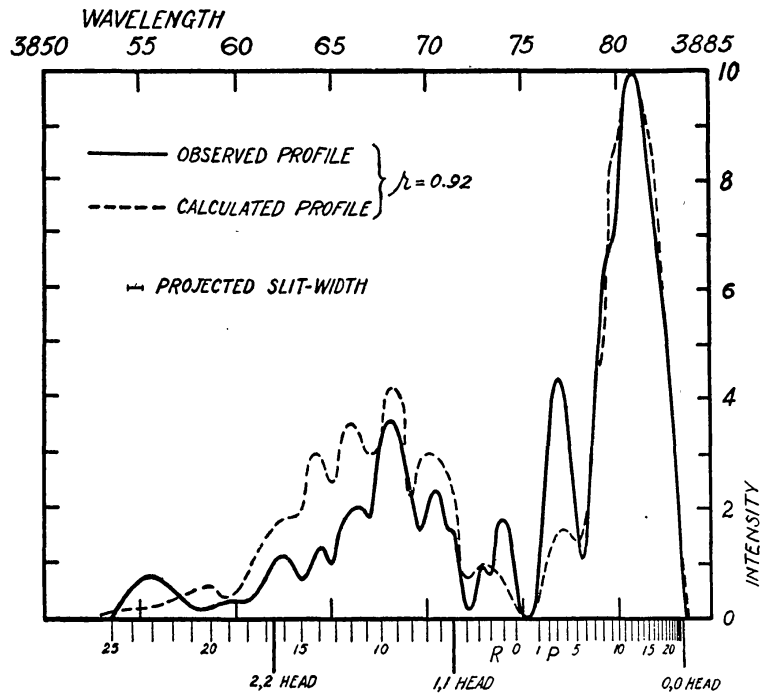


FIG. 4.—Observed and calculated profiles, CN bands, Comet 1940 c, $r = 0.92$.

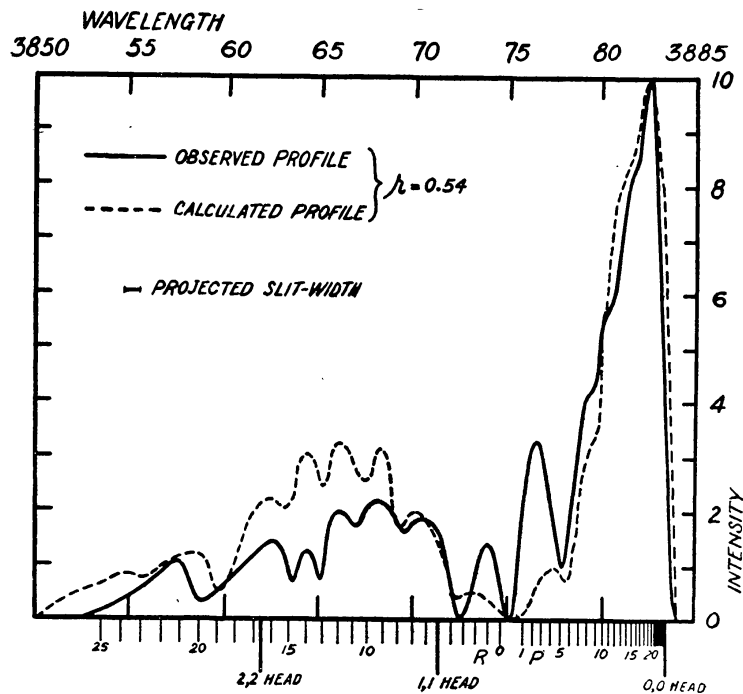


FIG. 5.—Observed and calculated profiles, CN bands, Comet 1940 c, $r = 0.54$.

but the characteristics of their spectra render the agreement between observation and theory less spectacular than for CN .

In the case of the identification of CH^+ , an examination of the intensity distribution in the exciting solar spectrum shows that the absorption transitions to the level $K' = 3$,

$v' = 0$ are more reduced by Fraunhofer lines than those corresponding to $K' = 2; v' = 0$. Hence the intensities of the bright lines $R(2)$, $Q(3)$ and $P(4)$ are reduced relative to those of $R(1)$, $Q(2)$ and $P(3)$ in the $(0, 0)$ band.

The identification of OH^+ is especially complex, not only on account of the proximity of the CN features, but also on account of the extremely complex profile of the solar spectrum in the region $\lambda\lambda$ 3565–3590. The intensity distribution among the OH^+ lines must certainly be very complex.

When the analysis of the laboratory spectra of CH_2 and NH_2 are completed, the discussion of the intensity distributions in the corresponding bands in the cometary spectra will be interesting. For example, in the solar spectrum a large number of strong absorption lines due to Mn , Fe and Mg appear in the region of the CH_2 group; especially the intense Fe lines $\lambda\lambda$ 4055.8 (solar intensity 30), 4063.6 (int. 20) and 4071.7 (int. 15). These should perturb the intensity distribution in the cometary CH_2 band.

All these considerations show that the work of identification of the features of cometary spectra must proceed with great caution. The final test of an identification should be based on the decomposition 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 too closely the intensity distribution in a laboratory spectrum, even of a low temperature source (52).

Distributions of Cometary Molecules in their Rotational and Vibrational Levels.—In the absence of collisional effects, the primary mechanism which is involved in populating

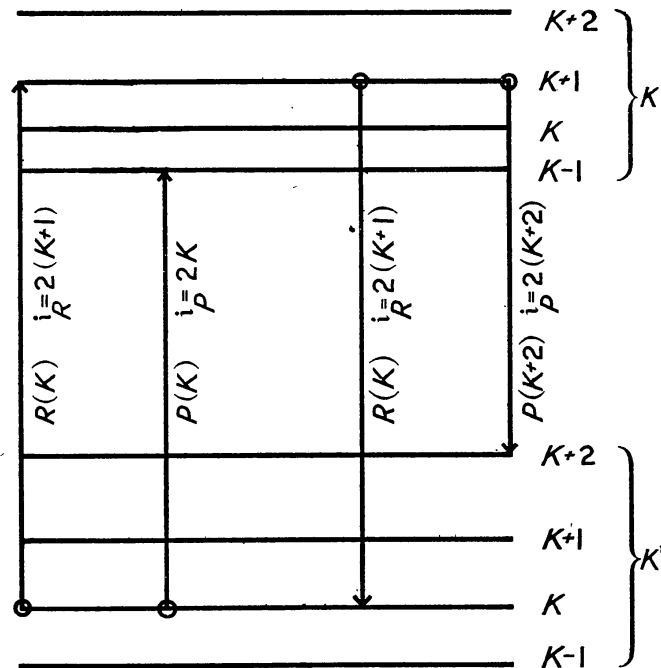


FIG. 6.—Transition probabilities in a $\Sigma \rightarrow \Sigma$ band.

the vibrational and rotational levels is the absorption of solar radiation. This point was emphasized by Wurm a few years ago (53), and is illustrated by the case of the rotational levels of a diatomic molecule, the corresponding band having no Q branch (fig. 6). In absorption, the $R(K)$ line is stronger than $P(K)$ (see the i -values in fig. 6): this tends to populate the higher K' levels in the excited electronic state. In the emission from level $K+1$, 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 the high-temperature type depends on the depopulating processes. Downward transitions between rotational levels belong to the pure rotational far infra-red spectrum. If this spectrum is permitted—which is the case for heteronuclear diatomic molecules—the downward transitions will be able to depopulate the K'' levels. Since the intensity ratios $K+1/K$ and $K+2/K+1$ decrease with K , the populating processes for high values of K become compensated by depopulating processes, the deciding factor being evidently the relative values of the time between successive absorption processes and the lifetime of the rotational states. This explains why the bands of CH , OH , NH , CN and CH^+ have, on the whole, low-temperature rotational distributions. Of course, beside the heliocentric distance, the individual characteristics of the molecules are of utmost importance in determining the actual distributions (53). These characteristics are mainly the dipole moments (and thus the mean lifetimes of the rotational states) 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 give bands of high-temperature rotational distributions. Considerations of a similar character apply to the vibrational levels.

On the basis of these general considerations we may understand why the profiles of the bands of the isotopic $C^{12}C^{13}$ molecule at $\lambda\lambda$ 4745, 4723 and 4706 are different from those of the corresponding bands of $C^{12}C^{12}$. Actually the bands of $C^{12}C^{13}$ are hazy, whereas the $C^{12}C^{12}$ bands have sharp edges. The difference of rotational intensity distribution in $C^{12}C^{12}$ and $C^{12}C^{13}$ is due to the fact that whereas the highly excited rotational levels of the ground electronic state of $C^{12}C^{12}$ 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 $C^{12}C^{13}$. In other words, the $C^{12}C^{12}$ bands would be reduced to the first lines of the branches at very large heliocentric distances only, whereas the depopulating process operates at much smaller heliocentric distances for $C^{12}C^{13}$.

Next we must consider the influence of the solar absorption lines on the populations of the rotational states. For example, if we start from molecules on the level $K''=K$ (fig. 6), and if $\lambda_{R(K)}$ coincides with a strong solar line, the population of level $K''=K+2$ will be reduced. It is easily seen that, as a result, a more or less irregular distribution amongst the rotational states K'' may be brought about. On the whole this tends to increase the contrast between subordinate maxima and minima in the rotational bands. It would explain why, in figs. 4 and 5, the contrast between the calculated maxima (at $K' \simeq 2$) and minima (at $K' \simeq 5$) in the P branch of the CN band is smaller than the observed contrast.

McKellar (54) has just completed a discussion of the rotational distribution of the CH molecules in the nucleus of Comet 1940 c. His result is that nearly all the molecules exist in the two lowest rotational levels, $K''=1$ and 2.

A rigorous theoretical treatment of this problem along the theory of cyclical transitions would be very desirable, especially for the CH molecules for which quantitative results have been obtained by McKellar.

These considerations illustrate the artificial character of the concepts of vibrational and rotational “temperatures” of cometary bands. As may be expected the “temperatures” obtained from different molecules may differ considerably. McKellar reported that the CN bands in Comet Cunningham correspond roughly to $T=435^\circ K$ for $r=0.54$, whereas for CH the temperature is only $200^\circ K$.

The general increase in “rotational temperature” with decreasing heliocentric distance is a well-established fact for the (0, 0) band of CN (55). Great care, however,

has to be exercised when discussing variations in rotational intensity distribution with heliocentric distance, since the change in radial velocity also affects the distribution.

Variations in rotational intensity distribution similar to those found for *CN* have also been observed for *OH*, *NH* and *CH*. For example, Table I shows the striking differences of rotational distribution in the *OH* band in different comets. In Comet 1941 *d* (r from 1.51 to 1.25, $dr/dt \simeq -22$ km./sec.) and in Comet 1942 *a* ($r \simeq 1.75$, $dr/dt \simeq -13$ km./sec.), the intensity distribution among the *OH* lines is very different from that in Comet 1940 *c* ($r \simeq 1$, $dr/dt \simeq -35$ km./sec.). In Comets 1942 *a* and 1941 *d* the lowest rotational levels of *OH* are favoured, as compared with Comet 1940 *c* (56). It can easily be seen that this is not due to the different radial velocity shifts of the exciting solar radiation, but rather to the different types of rotational distribution corresponding to the heliocentric distances.

Similar results have been obtained for *CH* (57) and *NH* (58), and it will be interesting later on to discuss the cases of *CH₂* and *NH₂*, once these spectra have been classified.

The vibrational distributions depend also on the heliocentric distance; this was proved to be true for heteronuclear molecules of low vibrational temperature, such as *CN* (59), as well as for the homonuclear molecule of high vibrational temperature, *C¹²C¹²* (60).

5. General Considerations on Cometary Physics

From the considerations of sections 1, 2 and 3, it appears that the following molecules have been identified in comets: *OH*, *NH*, *CN*, *CH*, *C₂*, *CH⁺*, *CH₂*, *CO⁺*, *N₂⁺* and probably *NH₂* and *OH⁺*. It is well known also that the *D* lines of *Na* appear at small heliocentric distances.

Beside the molecular bands and the *Na* lines, all the spectra of comets show a solar absorption spectrum (see Plate 4) which results from the reflection or scattering of solar light by the solid particles present, not only in the nucleus, but also in the head and even in the tail.

One may wonder how a "low-temperature source," like a cometary atmosphere, can contain radicals such as *OH*, *CH*, *CN*, *NH*, *C₂*, that are not chemically stable. Actually these compounds are physically stable, since their ground electronic state has an energy that is smaller than the energy of the separated atoms. Molecules are considered as chemically stable if they can exist for an appreciable length of time even when colliding with each other at low temperatures. *OH*, *CH*, *CN*, etc., are thus not chemically stable, but they may be present in cometary atmospheres because of the low densities prevailing in such atmospheres, and the consequent almost complete absence of collisions. Similarly, *CH*, *CN* and *CH⁺* are observed in another "low temperature gas" of very low density—the interstellar gas.

The molecules giving rise to the observed bands cannot exist as such in the occluded state in the cometary solid particles, since they are not chemically stable. They result from the photo-dissociation of more complex, chemically stable parent molecules, which were present in the solid particles as occluded gases and were set free by the action of solar radiation. Part of the chemically stable molecules must be polyatomic compounds of hydrogen, carbon, nitrogen, oxygen, sulphur, and possibly some other elements.

It is perhaps not entirely legitimate to assume for the solid parts of the cometary nuclei (at least for their occluded gases) a chemical constitution similar to that of the meteorites found on the earth. Yet, as a working hypothesis, it may help to relate the gaseous constituents of cometary atmospheres to the chemical natures of the occluded gases in the various types of meteorites. The gas released from meteorites by breaking or heating them in vacuum may sometimes amount to sixty times the volume of the meteorite itself. The gases which have been found in meteorites are (61) *CO₂*, *CO*, *CH₄*, *H₂*, *N₂*, *H₂S*, *SO₂*, and there is little doubt that comets must also contain *H₂O* and *NH₃*.

For a specific solar excitation, *i.e.* at a specific heliocentric distance and for a specific radial velocity of the comet relative to the Sun, the intensity ratio of the scattered solar spectrum to that 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 (62). Variations also occur among the occluded gases found in the different types of iron or stone meteorites (61), for example, the abundance ratio of CH_4 to CO (or CO_2) in stone meteorites differs considerably from the ratio in iron meteorites.

Each type of molecule has a definite range of extension in the head of the comet, corresponding to the mean free path before photo-dissociation or photo-ionization by solar radiation occurs. In order of increasing range of extension, we have the following sequence: CH , CH_2 and NH_2 (concentrated near the nucleus); OH ; NH ; CN and C_2 . The ionized molecules CH^+ , CO^+ and N_2^+ extend into the tail, but are observed in the head also, in the close neighbourhood of the nucleus. Our knowledge of the exact nature of the parent molecules and of the photo-dissociation and photo-ionization mechanisms is still very limited and vague. According to the Franck-Condon principle, a continuous absorption from the ground state, leading to the dissociation of the molecule, will be possible only if the nuclear distance r_e' in the upper electronic state is appreciably larger than that (r_e'') in the ground state. Cometary molecules may also be dissociated by absorption of solar light in a predissociation region of their spectrum. Accordingly, some predictions may be made with respect to the spectral regions of solar radiation that may dissociate specific molecules whose spectra have been analyzed in detail. In the case of C_2 , for example, an excited electronic state exists about 6 volts above the ground state; this excited level has a nuclear distance, r_e' , much larger than r_e'' . Thus the absorption of solar radiation of wave-length shorter than about λ 2000, by C_2 molecules, will lead to their dissociation. The ionization energy of C_2 is about 12 volts; and hence, as indicated by K. Wurm (65), the ionization process is negligible for C_2 , as compared with the efficiency of dissociation.

It may safely be assumed that the velocities of the various molecules in the comet's head originate mainly in the process of photo-dissociation of the parent molecules. When the gases occluded in the meteoritic nucleus are given off, they move away from the nucleus with velocities corresponding to their temperature in the nucleus. But the diatomic radicals resulting from the dissociation of these parent gases may move much more rapidly. As was shown by Wurm (65), this is illustrated by the extensions of CN and CO^+ . The fact that CO^+ may be driven off in the tail, by light-pressure, at considerable distances from the nucleus, proves that the average lifetime of CO^+ in the field of solar radiation is long. Yet in the head itself, the CO^+ molecules are observed only very near the nucleus, or behind it in the direction of the tail. Since the masses of CN and CO^+ are not very different, their thermal motions cannot be very different. Thus we must conclude that their different velocities near the nucleus—giving rise to their different extensions in the head—result from the photo-dissociation mechanisms.

Our ideas about the relative abundances of the various molecules are still very vague. The observed intensities depend on the abundances, the oscillator strengths f , and the intensity of the exciting solar radiation. We have more or less reliable laboratory values for $f(OH)$ (66), $f(CN)$ (67), and $f(CH)$ (68); and theoretical values for $f(NH)$ and $f(C_2)$ (69). At present we can say only that the abundances of these five molecules in comets are all of the same order of magnitude. For example, it is true that the OH bands are very weak compared with those of CN , but $f(OH)$ is also very small compared with $f(CN)$, and the solar radiation is much weaker near λ 3090 (OH absorption) than near λ 3880 (CN absorption). No f values are available at present for CH^+ , CO^+ , N_2^+ , OH^+ , but we may assume that the f values for these ions are similar to those of the corresponding electronic transitions in the iso-electronic neutral molecules. The oscillator strengths are also unknown for CH_2 and NH_2 .

Certain regions of a cometary head reveal CH molecules, both in the neutral and in

the ionized states. We do not know the relative oscillator strengths of CH and CH^+ , and no photometric determination has been made of the relative intensities of the CH and CH^+ bands. Hence it is impossible to estimate the average ionization of the CH molecules (70).

The ionization potentials of CO , N_2 and CH , and the corresponding wave-lengths, are:

for CO ,	$14.1 \pm 0.2 v$,	or $\lambda 880$;
for N_2 ,	$15.51 v$,	or $\lambda 800$;
for CH ,	$11.13 \pm 0.22 v$,	or $\lambda 1110$.

A direct photo-ionization of CO , N_2 and CH by solar radiation appears very improbable. If the Sun radiates like a black-body at $T \simeq 6000^\circ K$, its continuum must be very weak around $\lambda 1000$. 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. As for CH , its ionization limit falls about half-way between Lyman α ($\lambda 1216$) and Lyman β ($\lambda 1026$), 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 (71). Photo-dissociations of parent molecules into a positive and a negative ion are not excluded (71), but there is probably little we could say about it at present. Finally, ionization of CO , N_2 and CH in several steps, *via* intermediate (and possibly metastable) levels, may play a rôle.

Because of the low density and the small extension of the cometary regions common to CH and CH^+ , there is practically no possibility of capture of electrons by CH^+ ions. In other words, once a CH molecule has been able to absorb photo-electrically a solar photon of wave-length shorter than $\lambda 1110$, there is practically no chance of an electron being recaptured. Hence, great care must be exercised when considering ionization in comets.

Absorption by molecules of CH , CN and CH^+ is found in another astronomical source, the interstellar gas. The only difference is that the C_2 bands which are strong in comets are absent in interstellar absorption. This may be explained theoretically (72). The similarity in constitution between cometary and interstellar gases is simply a consequence of the cosmic abundances of the elements, and of the characteristic physical properties of the molecules.

Actually, the problems of molecular formation are quite different in comets and in interstellar gas. In comets the atmosphere is generated by the liberation of gases occluded in the meteorites forming the nucleus; the observed molecules result from the photo-dissociation of these parent gases, accompanied or followed by ionization. The interstellar molecules result from the association of two atoms.

Much observational work remains to be done on the spectra of different parts of the comets; as was emphasized by Bobrovnikoff (73). Spectrograms should be taken of the next bright and active comet by placing the slit on such formations as jets, fans, edges of envelopes, etc.

No attempt will be made here to review or discuss the dynamical and photometric problems of comets; for these the reader may refer to recent papers by Bobrovnikoff (73).

The general conclusion of this review is clear: despite the recent progress many questions remain to be answered before we can hope to reach a clear understanding of the physical chemistry of comets. The help of the physicist is especially desirable for the investigation of the spectra of CN^+ , C_2^+ , NH^+ , NH , etc., and for the determination of additional f values. A knowledge of the latter would make possible an estimation of the molecular abundances, and, as a result, a discussion of the photo-dissociation mechanisms in relation to heliocentric distance. Further investigations of the gases

occluded in meteorites of various types are desirable. Additional observations are also required in a number of fields, but especially spectroscopic observations in the red and near infra-red regions.

P. SWINGS

*McDonald and Yerkes Observatories :
1943 March.*

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- (44) S. Mrozowski, *Acta Physica Polonica*, 5, 85, 1936; *Rev. Mod. Phys.*, 14, 189, 1942.
- (45) *Lick Obs. Bull.*, 19, 131, 1941; *Pub. A.S.P.*, 54, 123, 1942.
- (46) *Rev. Mod. Phys.*, 14, 179, 1942; *Ap. J.*, 97, in press, 1943.
- (47) Since collisional effects are unimportant in cometary atmospheres, the rotational and vibrational intensity distributions of the bands attributed to a specific molecule result only from the distributions in the rotational and vibrational levels of the excited electronic state. The isotopes may also influence the structure, but this has been considered in section 2.
- (48) J. Dufay, *C.R.*, 206, 1948, 1938; Swings, Elvey and Babcock, *Ap. J.*, 94, 320, 1941.
- (49) Adel, *Pub. A.S.P.*, 49, 254, 1937; 50, 247, 1938; Wurm, *Zs. f. Ap.*, 15, 115, 1938; Wurm, *Ap. J.*, 89, 312, 1939; Swings and Nicolet, *Ap. J.*, 88, 173, 1938; McKellar, *Pub. A.S.P.*, 52, 283, 1940; V. M. Slipher, *Bull. Lowell Obs.*, 2, 67, 1914; 2, 151, 1916.
- (50) Minnaert, Mulders and Houtgast, Utrecht, 1940.
- (51) Swings and Nicolet, *Ap. J.*, 88, 173, 1938.
- (52) This procedure should actually be used generally in astrophysics whenever fluorescence is excited by radiation which differs considerably from a black-body continuum, this being in fact the general case. The exciting radiation contains usually either absorption lines, bands or continua, or emission features, and these are shifted to a certain extent with respect to the excited gas, because of relative velocities.

Typical examples of astronomical fluorescence are: (a) Specific incomplete multiplets of OIII and NIII may be excited in nebulae and similar objects, due to the coincidence of the resonance line of HeII with an absorption line of OIII, and another similar coincidence between OIII and NIII lines (Bowen's mechanism). The efficiency of this mechanism depends largely on the velocities of the layers emitting the HeII 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 OIII and NIII incomplete multiplets suddenly. (b) In shells surrounding stars of early type, peculiar selectivities are observed among the transitions in HeI (variations in relative intensities of the triplets and singlets in emission), NIII (presence of $3p^2P^0 - 3d^2D$ in emission, while $3s^2S - 3p^2P^0$ is present in absorption), CIII (presence of $3p^1P^0 - 3d^1D$ in emission, while $3s^2S - 3p^2P^0$ is in absorption), NIV (same as CIII), SiIII (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), SiII (absence of the usually strong doublet $3d^2D - 4f^2F^0$), NII, CII, FeII, 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