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COMPLEX STRUCTURE OF COMETARY BANDS TENTATIVELY ASCRIBED TO THE CONTOUR OF THE SOLAR SPECTRUM

BY

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Most of the bands observed in the spectra of cometary heads within the wave length range λ3000–λ6500 have been satisfactorily attributed to the molecules OH, NH, CN, CH and C_2,[1] the only remaining unidentified features being the "λ4050 group" and some bands of the visual region. These latter sets of lines have resisted all attempts at identification.[1] It seems likely that the interpretation of the "λ4050 group" will require additional laboratory work, the most promising line of approach being the investigations of the spectra of ionized diatomic molecules, especially NH^+, C_2^+, and CN^+. The recent theoretical and experimental investigations[2] on the oscillator strengths f of the molecules OH, NH, CN, CH and C_2, provisional though they are, provide an approximate idea regarding the abundances of the five molecules. There is fairly good agreement among the various investigators with regard to a low value of f (OH) compared to f (CN), and to an intermediate value of f (NH), whereas the case of f (CH) still remains unsettled. On the whole, it appears that the abundances of the five definitely identified molecules are of the same order of magnitude. The possibility of discovering new molecules depends at present on the identification of the "λ4050 group," of some features in the visual region, and upon the acquisition of new spectroscopic observations in the red and near infra red regions. An effort in the region from λ6000 A to λ10,000 A, with a dispersion of at least 100 A/mm would certainly provide information of considerable interest.

Despite the numerous cometary investigations published in recent years, few conclusions may be considered as satisfactorily established, particularly with regard to the physical processes involved in the liberation, and the simultaneous or subsequent excitation of the observed diatomic molecules. For the solution of these fundamental problems, several photometric investigations would be desirable: first, a discussion of the extensions of the molecules in the head, and of the variations of these extensions with heliocentric distance; second, a photometric investigation of the variations in relative intensities of the bands in different comets and at different heliocentric distances. Actually, only qualitative data are available at present in these two respects, and these may sometimes be misleading because of observational difficulties. A third promising approach is the interpretation of the rotational and vibrational intensity distribution in the molecular bands.

During my stay on Mount Hamilton, and through the courtesy of Director Wright, I have had access to the important collection of cometary spectra obtained by the Astronomers of the Lick Observatory, especially by Dr. Wright. On the basis of these spectrograms, and of observational results published by the McDonald Observatory Astronomers and by others, it is possible to describe more fully the present situation with respect to the structures of cometary bands, and to attempt to deduce some general conclusions. This is the object of the present paper.

Since collisional effects are unimportant in cometary atmospheres, the rotational and vibrational structures of the bands attributed to a given molecule result primarily from the distribution in the rotational and vibra-

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[1] Swings, Elvey and H. W. Babcock, *Ap.J.*, **94**, 320, 1941. J. Dufay has recently proposed to attribute the λ4050 group to Na H; but this identification is not convincing (private communication; probably published in the *C.R.*, Paris, 1941).

[2] Oldenberg and Rieke, *J. Chem. Phys.*, **6**, 439, 1938 (OH, experimental); J. U. White, *ibid.*, **8**, 79, 1940 (CN, exper.); R. S. Mulliken *Ap.J.*, **89**, 287, 1939 (theoretical); T. Dunham Jr., *Pub.A.A.S.*, **10**, 123, 1941 (CH and CN, exper.); Lyddane, Rogers and Roach, *Phys. Rev.* **60**, 281, 1941 (NH, CH and C_2, theoretical); R. S. Mulliken and Mrs. C. Rieke, private communication (OH, NH, CH, CN and C_2, theoretical).

tional levels of the excited electronic state, and only secondarily from the possible presence of isotopes. This secondary reason will be considered first.

Numerous spectroscopic investigations of the carbon stars, especially by Sanford[3] 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. Considering that the strong emission bands of the comets are the same as the intense absorption bands of the carbon stars, Bobrovnikoff[4] examined the Lick Observatory cometary spectra for evidence of bands due to $C^{12}\,C^{13}$. He observed a faint band at $\lambda 4744$[5] on several spectrograms of Comet Brooks and Comet Halley. Our new measurements of these spectrograms 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 1940c taken at the McDonald Observatory fail to reveal any trace of $\lambda 4744$, despite the fact that the ordinary Swan bands are sometimes strongly overexposed. 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[6] in meteoritic graphite and in ordinary Acheson graphite, failed to reveal any difference between the two samples.

No trace of the (0, 1) band of $C^{13}N^{14}$ could be detected (head at $\lambda 4208.4$, against $\lambda 4216.0$ for $C^{12}\,N^{14}$) either on the Lick, or on the McDonald cometary spectrograms. A systematic search for the isotopes of other elements, especially for deuterium, failed to reveal any isotope. This result indicates that no observed comet has presented abnormally high isotopic abundances compared to the earth. Therefore, except for bands of $C^{12}\,C^{13}$, the isotopes do not play an important role in the observed structures of cometary features.

It is well known that the rotational intensity distribution in the Swan bands of C_2 is very similar to a laboratory source at a temperature of the order of 3000° K. On the contrary only very low values of the rotational quantum number K' are observed for OH, NH, and CH ($K' \leqq 3$ for OH; $\leqq 2$ for NH; $\leqq 6$ for CH).[1] For CN, the observed K' may approach 20. The intensity distribution among the rotational lines of OH, NH and CH is roughly of the type which may be expected at a low temperature, say from about 100° K to 400° K. Quantitative photometric work has been reported only in the case of the CH band in Comet 1939 d; McKellar[7] found that the profiles of the CH band for r = 0.59 and $r = 0.83$ are similar to what would be expected in thermal equilibrium at temperatures of 250° K and 120° K respectively. No other photometric investigation of the profiles of the OH, NH or CH bands has been published.

A different situation obtains in the case of the CN molecules. If certain rotational lines are enhanced, their observation may be easier and their appearance more striking in CN, since the rotational lines are more closely packed than for the lighter molecules, and since larger values of K' are observed (up to about 20). Earlier work on the structure of the CN bands by Baldet, Bobrovnikoff, Wurm, Adel, Swings and Nicolet, Dufay, and McKellar has been reviewed recently.[1] The main conclusion of the McDonald observers on the basis of their spectrograms of Comet Cunningham was that the populations in the upper rotational levels K' are not distributed according to a law which gives but one maximum. There is a definite maximum around $K' = 2$ and 3, and another one for higher values of K'. Some McDonald spectrograms also revealed a doubling of the P head of the (0, 0) transition. Spectrograms of Comet Paraskevopoulos taken in February 1941 with a higher resolving power (dispersion at $\lambda 3870$: 44.5 A/mm; effective slit width 0.8A) revealed a still more complex structure.[8] A discussion of this structure indicates that a revision of the previous classification of the CN features observed in Comet Cunningham[1] is necessary, for it is now evident that more than two intensity maxima were present among the rotational lines.

Simultaneously, McKellar,[9] using spectrograms of great spectral purity obtained at Victoria (dispersion at $\lambda 3880$: 57 A/mm; effective slit width 0.8A) made the important observation that the rotational levels $K' = 2$, 7, 8 and 11 of the upper vibrational state are excessively populated.

In order to facilitate the general discussion of the possible mechanisms of excitation, we have collected a number of representative observational data. These will concern mainly the $\Delta v = 0$ sequence of CN which is much stronger and has been better observed (also with greater spectral purity) than the $\Delta v = -1$ sequence. In Table 1 will be found the observations of the $\Delta v = 0$ sequence (wave lengths in I.A. reduced to the Earth)

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[3] See f. ex. *Pub. A. S. P.*, **52**, 203, 1940.

[4] *Pub. A. S. P.*, **42**, 119, 1930.

[5] This would be the isotopic band most easily detected in cometary spectra. No solar intensity maximum could explain the observed band satisfactorily. Of course, it cannot be excluded that the observed feature may be due to an as yet unknown band.

[6] *Pub. A. S. P.*, **48**, 323, 1936.

[7] *Ibid.*, **52**, 283, 1940. In a recent letter, Dr. McKellar has informed me that he is engaged in a photometric investigation of the profiles in Comet Cunningham, Comet Jurlof and Comet Peltier.

[8] Elvey, Swings and H. W. Babcock, *Ap.J.*, in press.

[9] *Pub. A. S. P.*, **53**, 235, 1941.

TABLE 1

THE $\Delta v=0$ SEQUENCE OF CN IN VARIOUS COMETS

Parask.	Cunn.	Jurlof	Brooks	Daniel	Beliavsky	Halley	Delavan	Finsler
	3852.0 (0–1)							
	3854.0 (1)			54.7		55.2 (1)		
	3857.7 (2)							
3863.8* (1)	62.5 (3)		64. (1)	62.3		63.1§§§		
3866.6** (1)	67.5 (4)		67.0 (3)	67.6		69.0 (4)	66.4	
3869.6§ (3)	69.9 (4)		69.9 (3)	70.4		69.8 (5)	69.0	69.9‡ (5)
3873.2† (1)	73.5 (2)		73.0 (1)	74.0			71.8	73.8 (3n)
3876.8§§ (1–2)	76.8 (4)		77.4 (2)	77.0		76.3§§§		78.6 (3n)
3880.3†† (10)	80.2 (20)	79.5	80.5 (10)	79.6 (6)	80.0 (8)	79.5 (10)	80.5	83.1 (10)
3881.7*** (10)	82.0	81.4	81.8 (10)	82.2 (10)	82.2 (10)	81.8 (10)	81.5	

* From 62.2 to 64.4.
** From 65.3 to 67.7.
§ From 68.8 to 70.5.
† From 72.4 to 74.3.
§§ From 76.2 to 77.6.
†† From 79.1 to 80.9.
*** From 80.9 to 82.4.
§§§ End of band.
‡ Maximum of band extending on violet side to 3862.8.

TABLE 2

ADOPTED COMETARY WAVE LENGTHS FOR THE $\Delta v=0$ SEQUENCE OF CN AND CORRESPONDING LABORATORY LINES

Comets		Laboratory§				
λ	Int.	(0, 0) Transition		(1, 1) Transition		(2, 2) Transition
		P branch	R branch	P branch	R branch	P branch***
3852.0	0–1				R (15) 51.6 R (14) 52.4	
3854.4	1				R (12) 54.1 R (11) 54.9	P (2) 54.5
3857.7	2				R (8) 57.2 R (7) 57.9	P (8) 57.4 P (9) 57.8
3863.3	3		R (15) 63.4	P (1) 63.6		
3867.1	4		R (11) 66.8 R (10) 67.6	P (8) 67.0 P (9) 67.4		
3869.8	4		R (7) 69.9	P (16) 69.7 P (17) 69.9		
3873.2	2		R (3) 72.7 R (2) 73.4			
3877.0	4	P (3) 76.8 P (4) 77.3				
3880.0	20	P (10) 80.0*				
3881.8	20	P (15) 81.6** P (16) 81.9				

* From P (8) at λ3879.2 to P (12) at λ3880.7.
** From P (13) at λ3881.0 to P (18) at λ3882.3.
*** The P branch of the (2, 2) transition plays only a minor role in most comets. Even the (1, 1) transition is absent from certain comets.
§ The rotational quantum numbers are the values of K'' (lower electronic level). $K' = K'' - 1$ for the P branch and $K' = K'' + 1$ for the R branch.

in Comets Paraskevopoulos,[8] Cunningham,[10] Jurlof,[11] Brooks,[12] Daniel,[13] Beliavsky,[14] Halley,[15] Delavan,[16] Finsler.[17] In Comet Zlatinsky,[18] and in Comet Mellish,[19] maxima were observed respectively at λλ3863.8, 3868.3, 3881, and at λλ3870, 3879.2. The wave lengths finally adopted are given in Table 2, together with the nearest laboratory lines; this table may appear rather artificial, since the structures are somewhat different in various comets, but it will help in the discussion.

Intensity distribution in the P *Branch of the* (*o, o*) *transition.*—The observation of a possible splitting in the immediate neighborhood of the band head near λ3881 requires a fairly high spectral purity. This condition is especially well fulfilled in McKellar's spectrograms of Comet Cunningham and in the McDonald spectrograms of Comet Paraskevopoulos. But the doubling appears also on various Lick spectrograms, especially of Comets Beliavsky and Daniel. The profile does not appear to be the same in all comets. In the narrow region between λ3879.2 and λ3880.7, the wave length intervals between successive rotational lines do not decrease appreciably, so that the observed maximum really corresponds to an excess in intensity of the P line arising from $K' = 9$. In the region from λ3881.0 to λ3882.3, the decrease in separation between successive rotational lines would suggest that the maximum intensity is in the P transition from $K' = 14$. The splitting of the band head is quite definite on some spectrograms, and the intensity minimum is fairly deep; thus it appears impossible to explain the observations by assuming an unperturbed distribution on the K' levels from $K' \sim 7$ to $K' \sim 17$ similar to a thermal equilibrium. This is in agreement with McKellar's result,[7] whereas, on the basis of the McDonald spectrograms of lower spectral purity of Comet Cunningham, a single continuous distribution on the K' levels had seemed sufficient.[1]

As indicated in Tables 1 and 2, another very definite intensity maximum in the P branch appears for low values of K'(2 and 3), whereas a region of deep intensity minimum centers around $K' = 5$ and 6.

Intensity distribution in the R branch of the (*o, o*) *transition.*—This is somewhat complicated because of possible blending with the P branch of the (1, 1) transition. Nevertheless, the presence of a maximum of intensity for $K' = 3$ is quite conspicuous. In the spectrograms of Comet Paraskevopoulos taken in January 1941 at the McDonald Observatory[8] (heliocentric distance ~0.8 A. U.), the (1, 1) branch plays only a minor blending role, and the observed lines should be classified as follows (Table 3). It appears that the P and R branches have four maxima, corresponding respectively to $K' = 2$ or 3, 8, 11 and 15. A strong maximum at $K' = 8$ in Comet Paraskevopoulos is evidenced by the strong line of the R branch at λ3869.6. If the P branch of the (1, 1) transition contributed appreciably to λ3869.6, the corresponding but fainter line of the R branch should have been observed near λ3852.

TABLE 3

INTENSITY MAXIMA IN THE CN BAND OF COMET PARASKEVOPOULOS ($r = 0.8$)

Comet		Notation (band o, o)
λ	Int.	
3863.8	1	R (14) + R (15)
3866.6	1	R (11)
3869.6	3	R (7) + R (8)
3873.2	1	R (2)
3876.8	1–2	P (3)
3880.3	10	P (11)*
3881.7	10	P (15)**

* From P (8) to P (13)
** From P (13) to P (19)

A general average picture therefore would be that maxima appear in the (o, o) band for $K' = 2 + 3$, 8, 11 and 15, although such a distribution may not be identical in all comets. In any case, it would be impossible to represent the observed features as the superposition of several unperturbed intensity distributions corresponding to thermal equilibria at different temperatures.

Structure of the (*1, 1*) *transition.*—The structure of the P branch is complicated by the superposition of the R branch of (o, o), whereas R (1, 1) is slightly affected by the faint P (2. 2). The measured wave lengths of the three features to the violet of λ3860 (Table 2) are less accurate than the others, and definite data on the favored values of K' for $v' = 1$ are much less reliable than for $v' = 0$. There is no evidence that the lines corresponding to $K' = 2$ and 3 are favored for $v' = 1$.

Structure of the (*o, 1*) *transition.*[20]—Since the excited levels are the same as for the (o, o) transition, we should expect intensity maxima corresponding to the same values of K'. As a matter of fact, faint, sharp lines in the positions of P (2) + P (3) and R (2) are observed. Compared to the (o, o) transition, the data on the other maxima of (o, 1) are rather unsatisfactory, because of

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[10] Swings, Elvey and H. W. Babcock, *Ap.J.*, **94**, 320, 1941. McKellar's measures based on spectrograms of greater spectral purity have not yet been published.

[11] McKellar, *Pub. A. S. P.*, **52**, 283, 1940 (Abstract; the wave lengths of only the two strong maxima are given in this abstract.)

[12] W. H. Wright, *Lick Obs. Bull.*, **7**, 8, 1912, and additional measurements by the author.

[13] Campbell, *Ap.J.*, **28**, 229, 1908.

[14] Bobrovnikoff, *Pub. A. S. P.*, **43**, 61, 1931. In this paper, Bobrovnikoff called attention to the striking splitting of the head of the P branch.

[15] Bobrovnikoff, *Pub. Lick Obs.*, **17**, 309, 1931.

[16] Curtiss and McLaughlin, *Pub. U. Michigan*, **3**, 263, 1923.

[17] Minkowski, *Pub. A. S. P.*, **49**, 276, 1937.

[18] V. M. Slipher, *Lowell Obs. Bull.*, **2**, 67, 1914.

[19] V. M. Slipher, *ibid.*, **2**, 151, 1916.

[20] A slight revision should be made in the classification of the features observed in Comet Cunningham, between λ4164 and λ4216, as given in *Ap.J.*, **94**, 320, 1941. λ4197 and λ4193 belong simultaneously to R (o, 1) and P (1, 2); λ4180 is probably due to R (1, 2) and λ4164 to P (2, 3).

lower resolving power and lower intensity. But when these two factors are taken into account, the structure of (0, 1) agrees reasonably well with that of (0, 0).

Evolution of the CN *structure with heliocentric distance.*—This evolution is illustrated in Table 4, which concerns Comet 1940 *c*; the classification of the various features is in Table 2. It is clear that the (1, 1) band has increased in intensity compared to (0, 0); but no conspicuous variation appears in the relative intensities of the features attributed to (0, 0).

Comparison between the CN *bands of Comets 1940 c and 1941 c.*—As is apparent from Table 1, the relative intensities of λ3869.8 and λ3867.1 are quite different in comets Cunningham and Paraskevopoulos. Spectrograms obtained at the same heliocentric distance ($r = 0.80$) show λ3867.2 stronger than λ3869.8 in Comet Cunningham, whereas the opposite is true in Comet Paraskevopoulos. In Comets Brooks and Daniel, the two features have approximately the same intensity.

TABLE 4

EVOLUTION OF THE $\Delta v = 0$ SEQUENCE OF CN IN COMET 1940 *c*

Wave length	Intensities (T)							
	Dec. 9 $r = 1.01$	Dec. 10 0.99	Dec. 17 0.85	Dec. 23 0.73	Dec. 24 0.71	Dec. 25 0.69	Dec. 31 0.58	Jan. 3 0.52
3852.0								0–1
3854.5				1–0	1	1–0	2	1
3857.7			1–0	1	2	1	2	2
3863.3	1	1	3	3n	3n	3n	4n	2n
3867.2	2+3*	2+3*	5n	5n	5	5n**	4n	3
3869.8	3	3	3s	4s	4s	4s	2s	3
3873.3	2s	2s	2vs	2vs	2vs	2vs	2s	2vs
3877.0	3s	3s	4vs	4vs	4vs	4vs	4s	3vs
3880.0***	10	10	15	15	15	20	20	20
3881.8***			20	20	20			

* Probably double.

** Possibly double.

*** The effective slit width being 1.2 A, the separation can be seen only on certain plates with proper exposures.

(T) Abbreviations: s = sharp; vs = very sharp; n = nebulous.

Tentative interpretation of the multiple structure of the bands.—Several recently published attempts at interpretation have been reviewed by McKellar[7] and by Swings, Elvey, and Babcock.[1] They concern mostly either the photodissociation of molecules such as C_2N_2 or HCN, whose CN radicals are freed with certain specific rotational energies; or a peculiar excitation process similar to the selectivity observed by Herzberg in the laboratory (in exciting the CN bands in active nitrogen). Another agency will be suggested here.

In the physical conditions prevailing in cometary atmospheres, the molecular emission may result either from the photodissociation of a complex compound into an excited diatomic molecule and some residual component, or from the direct excitation of diatomic molecules by absorption of solar radiation. Let us assume that the second process plays the dominating role in the case of CN. The intensities of the two emission lines P $(K' + 1)$ and R $(K' - 1)$ arising from a given excited rotational level K' will depend on the population on level K' and on the respective transition probabilities. If the excitation results only from absorption of solar light, the population $N'_{k'}$ on level K' will be proportional to the following expression:

$$N'_{k'} \propto N''_{k'+1} \times p_P^{abs} \times I_P + N''_{k'-1} \times p_R^{abs} \times I_R\,, \qquad (1)$$

where

$N''_{k'-1}$ and $N''_{k'+1}$ are the populations in the rotational levels $K'' = K' - 1$ and $K'' = K' + 1$ of the ground electronic and vibrational state;

p_P^{abs} and p_R^{abs}, the probabilities of the absorption lines P $(K' + 1)$ and R $(K' - 1)$;

I_P and I_R, 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 the correction is of the order of ±0.25 A).

For the sake of simplicity, we may first assume that the distribution $N''_{k''}$ is a simple, continuous function of K'' with only one maximum (e.g. of the Boltzmann type). Then it is obvious from formula (1) that $N'_{k'}$ will essentially depend on the intensity distribution of the solar radiation I with wave length. The important effect of the Fraunhofer lines appears strikingly when one plots the wave lengths of the P and R lines on the Photometric Atlas of the Solar Spectrum[21] or on Rowland's Map of the Solar Spectrum. The deep minima in the solar spectrum in the region of P (6) and P (7), and between R (2) and R (7) are probably 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

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[21] Minnaert, Mulders and Houtgast, Utrecht, 1940. The instrumental profile (total broadening of an ideal monochromatic line by the combined influence of spectrograph, photographic plate, and recording apparatus) does not influence the results stated here.

spectrum, caused mainly by λ3878.02 (Fe I, lab. int. 400, ⊙ 8) and λ3878.57 (Fe I, lab. int. 300, ⊙ 7). Also P (5) usually falls in a solar spectral region fainter than that near P (4). Another intensity minimum occurs between P (9) and P (12). On the whole it appears possible to explain the observed structures by assuming a simple distribution among the rotational levels of the ground electronic and vibrational state, and by attributing the intensity maxima and minima to a solar excitation influenced by the Fraunhofer lines. A similar hypothesis had been suggested by Wurm[22] to explain the sharp, displaced band head.

If this agency plays the predominant role, the observed pattern should be considered as a superposition of "resonance doublets,"[23] each consisting of a P and an R line, and of intensities proportional to (1). The resulting superposition may be quite different from the pattern obtained by exciting with radiation of constant intensity over the wave length range considered. Precise photometric work will be required to determine, from the observed pattern, the rotational distribution on the ground electronic state. If this distribution is of the Boltzmann type, the corresponding "temperature" seems in any case to be of the order of 300° K.

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. Differences in chemical constitution are probably present among comets, and this might influence the structures if we assume several rotational distributions among the CN molecules. Yet it does seem likely that the difference between the CN structures of comets of similar heliocentric distance is mainly due to the difference in radial velocity. This may, of course, also be applied to one comet at different heliocentric distances.

Once the question of CN has been discussed, it is interesting to examine also the cases of OH, NH and CH. Among the absorption lines of OH which are of interest in comets, only λ3078.43 may often correspond to a more reduced excitation than the other lines. But since λ3078.43 is only one of several absorption transitions of similar probability, leading to $K' = 1$, the effect of its variation will not be very marked. Naturally, this does not exclude more conspicuous variations for exceptional radial velocities. The case of NH is more complex.[24] The excitation of the NH molecules through the Q_1 (1), Q_1 (2) and P_1 (2) transitions will always be reduced, compared with the excitation through the R_1 (0) and Q_2 (2) transitions. This is due to the fact that λλ3361.7 Q_1 (1), 3361.0 Q_1 (2) and 3369.1 P_1 (2) fall in a region where the intensity of the solar spectrum is reduced to about 45 per cent of the background. Similarly the excitation of the NH molecules through the P_1 (3) transition (λ3372) may often be reduced by a strong Fraunhofer line of Ni I at λ3371.99. An examination of the photometric atlas of the solar spectrum reveals that we may expect appreciable variations in the excitation, and consequently in the observed NH structure.

The case of CH is similar to NH. Whereas certain transitions fall in more intense regions of the solar spectrum, certain others (e.g. λ4300.3 and λ4339) always fall in a region reduced to about 55 per cent of the background. Others (e.g. λλ4292.1, 4296.6 and 4303.9) will fall in regions of considerably reduced intensity for certain radial velocities. The abnormally sharp decrease in intensity, when passing from $K' = 3$ to $K' = 4$ may be due to the favorable location of the lines P_1 (4), P_2 (4) and R_1 (2) as compared with P_1 (5), P_2 (5), R_1 (3) and R_2 (3). In this latter connection, the rôle played by the excitation through Q_1 and Q_2 transitions is complex, since the first lines of the Q_1 and Q_2 branches fall in a solar spectrum region of irregular intensity having pronounced minima (to 25 per cent of the background) and maxima (to 95 per cent). Despite the "averaging" effect of the excitation through the P and R branches, we may expect variations in the profile of the Q branch, λ4313, among comets having different radial velocities.

CONCLUSIONS

Except for probable bands of C^{12} C^{13}, isotopes do not influence the structure of molecular bands in cometary spectra. It is suggested that the observed peculiar intensity distribution among the rotational lines of CN may be due to the solar absorption lines which reduce the number of CN molecules excited by certain specific transitions. In such an excitation mechanism, the radial velocity of the Sun with respect to the comet plays a significant role. Similar considerations probably apply to the bands of OH, NH and CH.

In conclusion, I wish to express my great indebtedness to the Regents of the University of California, for an appointment as Alexander F. Morrison Research Associate in the Lick Observatory, and for the privilege of having access to the Observatory's collection of cometary spectra. The help rendered in many discussions with the Director and members of the staff is also heartily acknowledged.

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[22] *Zs.f. Aph.*, **5**, 10, 1932.

[23] See f. ex. P. Swings, *Liége Publ.* 198, 1936. For other types of electronic transitions, "resonance triplets" or "singlets" might be present.

[24] The NH lines at λλ3364.7, 3369.1, and 3372.1 belong to the (0,0) transition (lines $P_2(2)$, $P_1(2)$ and $P_1(3)$) and not to the (1, 1) band, as stated in *Ap.J.*, **94**, 320, 1941 (Table 4).