23. *Abundance of Molecules in Stellar Atmospheres*

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1. The knowledge of the physical states in stellar atmospheres is highly required for interpreting the observed characteristics of the stellar spectra. Accordingly, it seems quite natural to think that in cool stars the observed spectral features are essentially related with molecular dissociation in stellar atmospheres. That is to say, the study of the dissociation equilibria is the basis of our understanding of the atmospheres of late type stars, especially, of M, S, and C type stars. The first comprehensive study on this problem was that by Russell¹⁾ who showed that the observed molecular feature in cool stars can reasonably be understood on the basis of the dissociation theory. Next important studies on this problem were those by Fujita²⁾ who emphasized the importance of H:C:N:O abundance ratio for the spectral branching in cool stars. He has also shown that O/C ratio is an important factor to distinguish the physical characteristics between M and S type stars. In recent years, de Jager and Neven³⁾ have treated this problem with the modern values of molecular constants. Though the gross feature of the molecular spectra were understood by these works, still further studies should be indispensable by the following reasons: First, there is no a priori reason why we can confine our attention only to diatomic molecules and H₂O. Indeed, C₃ and SiC₂ were identified in cool carbon stars and this fact suggests the predominance of more stable polyatomic molecules. Second, some of the molecular features in stars are not fully satisfactorily understood yet. For example, the well known observation that C₂ intensities in carbon stars go through maximum at C5 spectral type has not been accounted for. This fact indicates that our understanding of the physical state in cool stars is still unsatisfactory. Third, for the quantitative study of various types of cool stars, detailed computations of molecular abundance for variety of values of H:C:N:O ratio are required.

2. We evaluated the dissociation constants of about hundred molecules, the most important compounds of which are given in Table I together with the dissociation energies adopted. The equilibrium compositions of forty-four molecules composed of H, C, N, and O atoms were calculated^{*)} for sixteen sets of values of H:C:N:O ratio which

^{*)} The computations were performed by the electronic computer, OKITAK 5090, of the Computation Center, University of Tokyo.

Table I. Dissociation energies adopted

Binding	D (ev)	Binding	D (ev)	Binding	D (ev)
H-H	4.476 (a)	C-C	6.12 (f)	N-H	3.8 (a)
O-H	4.40 (a)	C ₂ -H	5.72 (e)	NH-H	3.76 (h)
HO-H	5.10 (b)	C ₂ H-H	4.95 (e)	NH ₂ -H	4.51 (h)
O-O	5.115 (a)	C ₂ H ₂ -H	1.69 (e)	C-N	8.2 (a)
C-O	11.090 (a)	C ₂ H ₃ -H	4.51 (e)	H-CN	4.95 (i)
CO-O	5.45 (b)	C ₂ -C	7.74 (f)	CN-CN	4.86 (j)
H-CO	1.17 (c)	C ₃ -H	4.92 (g)	C ₂ -N	8.13 (k)
N-N	9.758 (a)	C ₃ H-H	3.12 (g)	C ₃ -N	7.39 (k)
C-H	3.47 (a)	C ₃ H ₂ -H	3.51 (g)	H-C ₃ N	3.97 (k)
CH-H	4.35 (d)	C ₃ -C	5.21 (g)	N-O	6.503 (a)
CH ₂ -H	4.80 (d)	C ₄ -H	5.90 (g)	SiC-C	8.7 (l)
CH ₃ -H	4.38 (e)	C ₄ H-H	4.09 (g)		

(a) G. Herzberg, Ref. (9).

(b) F. D. Rossini *et al.*: Circ. N. B. S., 500 (1952).

(c) K. Klein and L. J. Schoen: J. Chem. Phys., 24, 1094 (1956).

(d) H. Prophet: J. Chem. Phys., 38, 2345 (1963).

(e) B. E. Knox and H. B. Palmer: Chem. Rev., 61, 247 (1961).

(f) J. Drowart *et al.*: J. Chem. Phys., 31, 1131 (1959).

(g) M. Cowperthwaite and S. H. Bauer: J. Chem. Phys., 36, 1743 (1962).

(h) A. P. Altshuller: J. Chem. Phys., 22, 1947 (1954).

(i) C. A. McDowell and J. M. Warren: Trans. Farad. Soc., 48, 1084 (1952).

(j) W. Tsang *et al.*: J. Chem. Phys., 36, 1768 (1962).(k) V. H. Dibeler *et al.*: J. Am. Chem. Soc., 83, 1813 (1961).(l) J. Drowart *et al.*: J. Chem. Phys., 29, 1015 (1958).

may cover the possible abundance ratio in cool stars such as M, MS, S, SC, C, CH, and hydrogen deficient stars. The computations were performed for the range of $\Xi=0.6\sim 5.0$ and $\log Pg \simeq -3.0\sim 8.0$ to be used for the quantitative analysis of stellar spectra, for the investigation of the atmospheric structures and also for the studies of the physical characteristics of cool stars as well as of general astrophysical problems. In what follows, we shall discuss briefly the main results.*)

3. We shall first discuss the equilibria in carbon rich stars. Fig. 1 shows the result for the abundance ratio of $H:C:N:O=10^3:5:5:1$ and $\log Pg \sim 3.0$. It should be noted that the polyatomic species such as HCN, C₂H and C₂H₂ etc. are more abundant than diatomic ones such as CN, CH, and C₂ especially below 2800°K. Though not shown in the figure, other species such as C₂N, C₃N, HC₃N and many

*) The details of the calculated results and their discussion in connection with observations, together with the discussions on molecular constants adopted, will be published in Annals of the Tokyo Astronomical Observatory.

Fig. 1. The equilibrium composition in carbon rich giants ($\log P_g \sim 3.0$). The logarithm of the partial pressure of atoms and molecules is plotted against $\Theta = 5040/T$.

hydrocarbons are also conspicuous. The overall feature of molecular equilibria is essentially controlled by polyatomic molecules rather than by diatomic ones in cool carbon stars.

It is interesting to note that C_2 concentration goes through maximum at about $2800^\circ K$, which may correspond to C5 spectral class. This fact can be regarded as the final justification to show the validity of C-classification by Keenan and Morgan⁴⁾ as a temperature class. The concentration of C_3 molecules to which one ascribes the source of enormous absorption in ultraviolet region of the spectra in cool carbon stars has also maximum at about $2800^\circ K$. This result offers the natural explanation to the observed fact that the so-called ultraviolet depression is by no means most intense in the coolest carbon stars but rather intense at C5~C6 spectral classes.⁵⁾ The reason why C_2 and C_3 concentrations pass through maximum at about $2800^\circ K$ is that the free carbons are largely depleted by HCN, C_2H , and C_2H_2 etc. below $2800^\circ K$. In this way, the molecular features of carbon stars are reasonably understood and this fact in turn is an indirect evidence to indicate the importance of polyatomic species not yet observed directly.

At high temperature, partial pressure of free carbon is proportional to gas pressure but, below $2800^\circ K$ ($\log P_g \sim 3.0$), it is almost independent of total gas pressure. This fact can be understood by the strengthened depletion of carbon atoms by HCN and C_2H_2 etc. at higher gas pressures. Then, the mass fraction of C_2 is larger for low luminosity at later C-type stars while smaller at early C-type stars. This fact will produce complicated absolute magnitude effect in observed C_2 intensities. The C_2 concentration is influenced by C/O ratios as was expected and our calculations for various N/C ratios for fixed H:C:O ratio also produces large scattering in C_2 concentrations.*¹⁾ In this way, the interpretation of the second parameter of C-classification by Keenan and Morgan⁴⁾ which was tentatively ascribed to the variations of C/O ratio, must be reinterpreted in future in terms of H:C:N:O ratio and luminosity.

In Fig. 1 is also shown the concentration of SiC_2 which was identified as the carrier of the so-called MS bands.⁶⁾ Though not shown in the figure, we have considered fifteen silicon compounds**¹⁾ to

*¹⁾ If $N/C > 1$, carbon atoms are largely depleted by HCN and C_2 concentration suffers large depletion while if $N/C < 1$, carbon atoms are no longer so strongly depleted by highly stable HCN but partial pressure of free carbon is mainly controlled by the equilibrium of hydrocarbons such as C_2H , C_2H_2 , and C_3H . It is also remarked, however, that the temperature at which C_2 concentration attains maximum is almost independent of H:C:N:O ratio so long as $C > O$ but depends only on total gas pressures.

**¹⁾ These are SiH , SiH_2 , SiH_3 , SiH_4 , SiC , SiC_2 , Si_2C , Si_2C_2 , Si_2C_3 , Si_3C_2 , SiN , SiO , SiO_2 , Si_2 , and Si_3 .

evaluate the concentration of SiC_2 . However, the results seem to be in contradiction with observations which show the decrease of MS band intensities for later C-type stars.⁷⁾ It is supposed that some unknown stable compounds such as HSiN , and Si_2H_2 etc. are present in carbon stars to deplete the silicon atoms in later C-type stars.

The straight line in Fig. 1 represents the saturated vapour pressure of graphite.⁸⁾ The partial pressure of free carbon exceeds the saturated vapour pressure of graphite at about 2200°K . This fact opens the possibility of precipitation of graphite particles. The equilibrium shown in Fig. 1 is a kind of pseudo equilibrium in which free carbon is supersaturated. At the strict thermal equilibrium, carbon atoms are condensed in graphite until partial pressure of free carbon is reduced to the value of saturated vapour pressure. Then, the concentrations of molecules containing carbon atoms which were in equilibrium with free carbon also suffer the large depletions.*)

4. For oxygen rich stars, the essential feature of molecular equilibria is not radically altered from those hitherto considered. Here, H_2O plays decisive role below 2500°K ($\log P_g \sim 3.0$). For M-dwarf stars, however, polyatomic species such as CH_2 , CH_3 , CH_4 , NH_2 , HCO , HCN , and CO_2 etc. are conspicuous, and at $\log P_g \sim 6.0$ and NH_3 , $T \sim 1000^\circ\text{K}$, carbon atoms are depleted by CH_4 rather than by CO even though $\text{O} > \text{C}$.

5. It is shown that polyatomic molecules are more important than those hitherto considered, especially in the atmospheres of cool carbon stars. It is evident that no consideration on dissociation equilibria in stellar atmospheres can be satisfactory which do not properly incorporate the part played by the polyatomic molecules. As forty-four molecules composed of H, C, N, and O atoms were considered, we may not be far from reality so long as the equilibria of compounds composed of H, C, N, and O atoms are concerned.

One may regard our results still of preliminary character in that the abundance of H, C, N and O atoms are not known at present. However, it should be emphasized that one of the very purposes of our study of molecular equilibria is to offer the basis of the quantitative analysis of molecular spectra by which the knowledge on abundance should be obtained.**)

*) At strict thermal equilibrium, below 2200°K , about 80% of carbon atoms are condensed in graphite, about 20% of carbons remain in CO molecules and very small fraction of total carbons are distributed among various compounds, which are in equilibrium with the free carbons, the concentration of which corresponds to saturated vapour pressure.

**) If one is to try to determine, for example, the N/C ratio in carbon stars from the observed CN/C_2 ratio, as the concentrations of CN and C_2 are influenced in complicated fashion by H:C:N:O ratio through the depletions of H, C, N, and O atoms by unobservable molecules such as CO , N_2 , HCN , and C_2H_2 etc., one must carefully compare the detailed calculations for many sets of values of H:C:N:O ratio with observations.

Our results show the predominance of polyatomic molecules in cool stars. However, the polyatomic compounds so far identified are only SiC_2 and C_3 . As was discussed by Herzberg,⁹⁾ the electronic spectra of polyatomic free radicals can possibly be observed in the visible spectral regions. It must be interesting to examine the identifications of abundant free radicals such as CH_2 , C_2H , C_3H , C_2N , and C_3N etc. in carbon stars as well as NH_2 , HCO , and CH_2 etc. in M-dwarf stars.

In view of the astrophysical significance, however, much attention should be directed to the rotation-vibration bands of polyatomic molecules in infrared region. As was pointed out by Wildt,¹⁰⁾ complex band absorptions aroused by many combinations of fundamentals as well as harmonics of molecular vibration of polyatomic molecules dominate the infrared region where large portion of the radiation flux of cool stars is concentrated, and hence the blanketing effect by them will play an essential role in determining the structure of stellar atmospheres. These effects may be important especially below 2800°K in giant stars. For M type stars, Yamashita¹¹⁾ has shown that the blanketing effect by H_2O is indeed important especially in late M stars. For carbon stars, polyatomic species are more numerous than in M stars and the blanketing effect by them, especially by HCN , C_2H_2 , CH_4 , and other hydrocarbons should be very important. If graphite particles are precipitated, they will also be important as a source of opacity. For exploring the atmospheres of carbon stars, much works must be done both in laboratory physics as well as in astrophysical observations and the roles played by the polyatomic molecules and by graphite particles should be clarified.

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References

- 1) H. N. Russell: *Ap. J.*, **79**, 317 (1934).
- 2) Y. Fujita: *Jap. Jour. Astr. and Geophys.*, **13**, 21 (1935); **17**, 17 (1939); **18**, 45 (1940); **18**, 177 (1941); *P. A. S. Japan*, **1**, 171 (1950).
- 3) C. de Jager and L. Neven: *Mém. Soc. R. Sc. Liège*, **18**, 357 (1957).
- 4) P. C. Keenan and W. W. Morgan: *Ap. J.*, **94**, 501 (1941).
- 5) A. Mckellar and E. H. Richardson: *Mém. Soc. R. Sc. Liège* **15**, 256 (1955).
- 6) B. Klemm: *Ap. J.*, **123**, 162 (1956).
- 7) J. Humblet and G. Mannino: *Ann. d' Ap.*, **18**, 321 (1955).
Y. Fujita *et al.*: *Publ. Dom. Astr. Obs.*, in press.
- 8) K. S. Pitzer and E. Clementi: *J. Am. Chem. Soc.*, **81**, 4778 (1959).
- 9) G. Herzberg: *Mém. Soc. R. Sc. Liège*, **18**, 397 (1957).
- 10) R. Wildt: *Mém. Soc. R. Sc. Liège*, **18**, 319 (1957).
- 11) Y. Yamashita: *P. A. S. Japan*, **14**, 390 (1962).