

RESEARCH ARTICLE | APRIL 01 1949

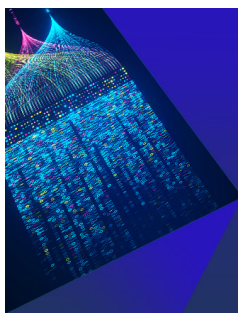
Errata: Rate of Nucleation in Condensed Systems FREE

J. C. Fisher



J. Chem. Phys. 17, 429 (1949)

<https://doi.org/10.1063/1.1747279>



Chemical Physics Reviews

**Special Topic: AI and Machine Learning
in Chemical and Materials Science**

Submit Today



is suggested by the resemblance to cellular convection,³ which has been treated successfully as a stability problem.⁴ A connection between cellular convection and combustion phenomena has been anticipated by Chandrasekhar.⁵ Instability of an infinitely thin plane flame front, taken as a surface of discontinuity of normal velocity and density in incompressible and inviscid flow has been established.⁶ This treatment cannot explain, however, the finite size of the cells and the existence of limits of composition beyond which the cell structure disappears. A theory in which the finite thickness of the combustion zone is taken into account is being developed.⁷ Dimensional analysis shows that in such a treatment the diameter of the cells should be proportional to the thickness of the combustion zone under otherwise unchanged conditions. Since a reduction of pressure causes an increase of combustion zone thickness without affecting other variables to a large extent, exploratory observations of cellular flames burning under reduced pressure have been performed in the Cornell Aeronautical Laboratory Altitude Chamber. The size of the cells was found to vary roughly inversely proportional to pressure, in accordance with the above-mentioned theoretical conclusion.

* This work was supported by the U. S. Navy under Project SQUID.

¹ H. F. Coward and G. W. Jones, U. S. Bur. of Mines Bull. 279, 65 (1938).

² F. A. Smith and S. F. Pickering, J. Research Nat. Bur. Stand. 3, 65 (1929).

³ H. Bénard, *Revue générale des Sciences* 12, 1261, 1309 (1900).

⁴ Lord Rayleigh, *Phil. Mag.* 32, 529 (1916), and others.

⁵ S. Chandrasekhar, *Meetings on Fundamentals of Combustion*, Applied Physics Laboratory, Johns Hopkins University, March 1947.

⁶ L. Landau, *Acta Physicochimica URSS* 19, 77 (1944).

⁷ H. Einbinder, forthcoming paper.

Errata: Rate of Nucleation in Condensed Systems

[J. Chem. Phys. 17, 71 (1949)]

J. C. FISHER

General Electric Company Research Laboratory, Schenectady, New York

THE first line of the second column, page 71, should end

$$i^* = (2A/3B)^3,$$

and Eq. (15) should read

$$R = n \int_{i_0}^{\infty} \exp(\Delta F_i/kT) i^{-3} di.$$

On the Electric Dipole Moment and Vibrational States of H₂B¹⁰CO*

M. W. P. STRANDBERG, C. S. PEARSALL, AND M. T. WEISS

Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts

February 18, 1949

THE $J=1 \rightarrow 2$ rotation absorption due to boron carbonyl has been observed by Gordy, Ring, and Burg,¹ from which they deduce a value of 3 for the B¹⁰ spin.

We have observed the $J=0 \rightarrow 1$ rotational transition in H₂B¹⁰CO for the ground vibrational state, and for two excited vibrational states (v_1, v_2), with negative α 's but as yet unassigned. The quadrupole hyperfine structure was not observed, since at room temperature ($\sim 23^\circ\text{C}$), the compound decomposed so rapidly (\sim a few seconds) under pumping, that lines less than 1 Mc/sec. could not be observed. The Stark effect was measured for two of the unresolved lines. The relevant data may be listed as follows:

H ₂ B ¹⁰ C ¹² O ¹⁶	$\nu_{J=0 \rightarrow 1}$	= 17,961.20 ± 0.05 Mc/sec.
	B ₀	= 8980.36 ± 0.025 Mc/sec.
	B _{0v1}	= 9002.66 ± 0.03 Mc/sec.
	B _{0v2}	= 8985.80 ± 0.03 Mc/sec.
	D _J	= 0.177 ± 0.03 Mc/sec.
	($\mu_{J=0 \rightarrow 1}$) ₀	= 1.795 ± 0.01 debye
	($\mu_{J=0 \rightarrow 1}$) _{v1}	= 1.770 ± 0.01 debye
	γ_0/γ_{v1}	≈ 3.
	γ_0/γ_{v2}	≈ 10.

These measurements were made with a spectroscope which we have been using for some time, and which exhibits high sensitivity. The system combines a modified f-m method² with a Stark detection scheme.³ The oscillator source is frequency-modulated at a frequency greater than the line breadth (instead of less than the line breadth as is usual), and of an amplitude such that the modulation index $m = \Delta f/f \approx 1$. This gives a carrier with essentially two strong sidebands at $\pm f$ from the carrier. A strong square-wave Stark field at about 6-kc/sec. repetition rate is imposed on the gas sample. The microwave field transmitted through the absorption sample is detected in a silicon crystal and amplified by a receiver tuned to the frequency-modulation rate, f , ± 6 kc/sec. The detected receiver output is further amplified in a narrow-band 6-kc/sec. amplifier. The theory of operation will be published later but, briefly, the high frequency f-m allows superheterodyne amplification with detection removed from the low frequency region of high crystal noise. In all detection processes, phase is preserved, so that band width narrowing at 6 kc/sec. increases the signal-to-noise power ratio by an amount inversely proportional to the band width. The band widths used by us are about 3 c.p.s., 10 c.p.s., and 800 c.p.s., and are stable since a phase-sensitive detector at 6 kc/sec. is used. The near d.c. signals (with 3- and 10-c.p.s. band widths) are remodulated to 6 kc/sec. and are displayed on a long-persistence (P7 screen) cathode-ray oscilloscope. The sensitivity has not been accurately checked except on the 800-c.p.s. band width, where $\alpha_{\text{min.}} \approx 5 \times 10^{-8}$. The 10-c.p.s. band width has been checked against that for 800 c.p.s., and the expected tenfold increase seems achieved. This means that with the 10-c.p.s. system, and $\alpha_{\text{min.}}$ of about 5×10^{-9} with oscilloscope presentation may be achieved.

We would like to acknowledge the use of a sample of diborane kindly supplied by G. B. Kistiakowsky and H. S. Gutowsky of Harvard University and the University of Illinois.

* This work has been supported in part by the Signal Corps, the Air Materiel Command, and ONR.

¹ W. Gordy, H. Ring, and A. Burg, *Phys. Rev.* 74, 1191 (1948).

² W. D. Hersberger, *J. App. Phys.* 19, 411 (1948).

³ R. H. Hughes and E. B. Wilson, *Phys. Rev.* 71, 562 (1947).

The Unsteady Shock Wave

BRUNO W. AUGENSTEIN

School of Aeronautics, Purdue University, Lafayette, Indiana

January 28, 1949

THE following comments concern the Letter to the Editor of F. Cap, entitled "A new equation for the non-stationary shock wave" (*J. Chem. Phys.* 17, 106, (1949)). The letter contains numerous misprints which make the equations and results unintelligible. In particular, the symbol u has throughout been used for both the particle speed before the wave, and for the ratio of specific heats, C_P/C_V .

Since the results obtained are of interest, a very brief alternative derivation is given here. If, as in the letter of Cap, we denote by w the wave speed relative to the gas in front of it, by u the particle speed, by P the pressure, by a the speed of sound, by $\gamma = C_P/C_V$ the ratio of specific heats, and if we use a subscript (₀) to denote states before the wave, and the subscript (_s) to denote the states after the wave, then it is known that the following relations hold for the unsteady shock:¹

$$\left(\frac{w}{a_0}\right)^2 = \frac{1}{2\gamma_0} \frac{(\lambda-1)[(\gamma_s+1)\lambda+(\gamma_s-1)]}{\lambda - [(\gamma_s-1)/(\gamma_0-1)]},$$

$$\left(\frac{a_s}{a_0}\right)^2 = \frac{\gamma_s \lambda (\gamma_s-1)\lambda + (\gamma_s-1) + 2[(\gamma_s-1)/(\gamma_0-1)]}{(\gamma_s+1)\lambda + (\gamma_s-1)}, \quad (1)$$

$$\left(\frac{u_s - u_0}{a_0}\right)^2 = \frac{2}{\gamma_0} \frac{(\lambda-1)(\lambda - [(\gamma_s-1)/(\gamma_0-1)])}{(\gamma_s+1)\lambda + (\gamma_s-1)},$$

where we have put: $\lambda = (P_s/P_0)$. For the limiting case of intense shock waves, $\lambda \rightarrow \infty$, we derive from Eq. (1) putting $u_0 = 0$, the following relations:

$$\begin{aligned} (u_s/a_s)^2 &= (2/\gamma_s(\gamma_s-1)), \\ (w/a_s)^2 &= [(\gamma_s+1)^2/2\gamma_s(\gamma_s-1)], \\ (w/u_s)^2 &= (\gamma_s+1/2)^2 = (w/a_s \cdot a_s/u_s)^2. \end{aligned} \quad (2)$$

For the case where $\gamma_0 = \gamma_s = 1.4$, we have, therefore:

$$u_s/a_s = 1.89, \quad w/a_s = 2.27, \quad w/u_s = 1.20, \quad (3)$$

and these are the results of the last line of the letter of Cap, as it should read. It is not to be implied that it is necessarily correct that $\gamma_s = \gamma_0$ is compatible with $\lambda \rightarrow \infty$. To answer such questions, the detailed structure of the shock wave and its wake must be investigated. Such questions and related ones are satisfactorily treated only by the higher order approximations of kinetic theory; an account of the techniques involved is given in reference 2. Relations (1) are derived under the assumption of a perfect gas equation of state, and zero relaxation time for all degrees of freedom of the gas swept over by the shock wave.

¹ H. Pfriem, *Forsch. Ing. Wesen. Bd.*, 12 (1941).

² S. Chapman and T. G. Cowling, *Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, London, 1939).

The Infra-Red Absorption Spectrum of *n*-Butane in the Solid State*

D. W. E. AXFORD AND D. H. RANK

Physics Department, Pennsylvania State College, State College, Pennsylvania

February 21, 1949

A SERIES of investigations,¹⁻⁴ carried out recently in this laboratory, on the Raman spectra of the normal hydrocarbons has established the co-existence of rotational isomers in the liquid phase and has demonstrated that only one of the isomers persists, in general, on solidification. Since there is no reason to doubt that the infra-red spectra would show a similar behavior, we have attempted to obtain the spectrum of solid *n*-butane in the hope of obtaining a corresponding simplification.

Previous investigations of infra-red spectra of organic compounds at low temperatures are few in number. Avery and Ellis⁵ studied the spectra of several simple hydrocarbons, including ethane, at liquid air temperature. Halford *et al.*^{6,7} have studied the spectrum of benzene and cyclohexane at low temperature, and Thompson and his co-workers⁸ have recently studied a considerable number of compounds in the liquid and solid states with a view to obtaining information about the effect of state of aggregation on the spectra.

The cell employed was based on a design at present being used by Dr. R. C. Lord at the Massachusetts Institute of Technology. It consists in essence of an ordinary infra-red absorption cell for liquids, with silver chloride windows, suspended inside an evacuated container, also with silver chloride windows. By cooling with liquid air it was possible to freeze the liquids completely and obtain a satisfactory spectrum of the frozen substance. The method probably does not allow a very accurate determination of percentage transmission because the liquid may leave gaps on freezing, but it is quite adequate to observe the general character of the spectra. In order to fill the cell with *n*-butane which boils at -0.3°C , it was necessary to cool the cell in dry ice before filling it and placing it in the outer jacket. However, with a little practice, this proved to be a fairly simple operation. The spectrometer

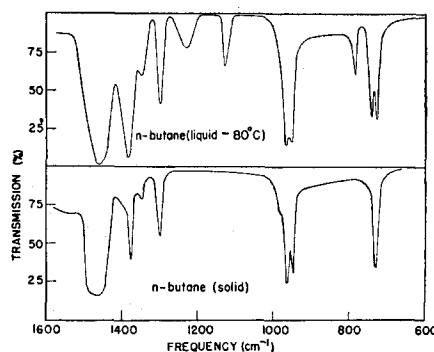


Fig. 1. Infra-red absorption spectrum of liquid *n*-butane at -80°C and solid *n*-butane at liquid air temperatures. Cell thickness 0.1 mm.

employed was a standard Perkin-Elmer instrument, Model 12c, used in conjunction with a Brown recorder.

The infra-red spectrum of gaseous *n*-butane is available,⁹ but not so that of the liquid, so we carried out experiments at -78°C also in order to get a trace for liquid *n*-butane. The traces for the liquid and solid are shown in Fig. 1. The spectra were investigated in the regions 7.5–14 μ since it is in this region that the most interesting changes are likely to occur on solidification.

The bands observable in the liquid and solid are listed below.

Gas ⁹ cm ⁻¹	Liquid cm ⁻¹	Solid cm ⁻¹
1466(s)	1462(s)	1461(s)
1390(s)	1392(s)	1382(s)
1340(w)	1350(w)	1350(w)
1297(s)	1297(m)	1299(m)
1244(w)	1233(w)	—
1134(m)	1133(m)	—
—	—	984(w)
970(s)	971(s)	965(s)
959(s)	961(s)	951(s)
795(w)	788(m)	—
751(m)	747(s)	—
734(m)	731(s)	732(s)

Our results agree well with conclusions already made¹ about the symmetry of the more stable isomer. The existence of, at the most, 8 lines in the infra-red where 10 are permitted in this region on the basis of the C_{2h} symmetry, is good evidence for the *trans*-isomer being the one formed on solidification. A few minor modifications in the assignment already made are required:

- (1) The frequency 732 cm^{-1} belongs to the low energy *trans*-form, not 751 cm^{-1} , as previously had been arbitrarily suggested.
- (2) It would appear likely that, since the bands at 1340 and 795 cm^{-1} disappear on cooling, they correspond to the less stable isomeric molecule rather than that they are summation or difference bands. However, this might occur due to the disappearance of one or both of the combining frequencies, and until data in the region below 650 cm^{-1} is available, this point cannot be unambiguously decided. In view, however, of their intensity in the liquid, we are inclined to assign them to the weak isomer.
- (3) There is no doubt that both the bands at 970 and 959 cm^{-1} belong to the *trans*-isomer. The only curious feature of the solid spectrum is the appearance of a marked shoulder at 988 cm^{-1} which is not detected in the gas or liquid. This may be because in the liquid and gaseous states it is obscured in the broad contour of the 970–951 cm^{-1} band. It is apparently genuine, as it was obtained on three separate occasions.

The results with *n*-butane show that the infra-red spectra of the solid supports the conclusions made previously. Experiments which we have made with the straight-chain hydrocarbons up to C_7 also show simplification in the spectra on freezing. It is intended to publish a full account of this work directly.

* This research was carried out on contract N6onr-269, Task Order V of ONR.

¹ Szasz, Sheppard, and Rank, *J. Chem. Phys.* **16**, 704 (1948).

² Rank, Sheppard, and Szasz, *J. Chem. Phys.* **17**, 83 (1949).

³ N. Sheppard and G. Szasz, *J. Chem. Phys.* **17**, 86 (1949).

⁴ G. Szasz and N. Sheppard, *J. Chem. Phys.* **17**, 93 (1949).

⁵ W. M. Avery and C. F. Ellis, *J. Chem. Phys.* **10**, 10 (1942).

⁶ R. S. Halford and G. B. Carpenter, *J. Chem. Phys.* **15**, 99 (1947).

⁷ R. S. Halford and O. A. Schaeffer, *J. Chem. Phys.* **14**, 141 (1946).

⁸ R. E. Richards and H. W. Thompson, *Proc. Roy. Soc. (London)* **195**, 1 (1948).