

Supersonic Dispersion and Absorption in CO₂

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Since supersonic velocity determinations in air near a crystal oscillator usually yield values in excess of the accepted value, $V_0 = 331.6$ m/sec., a similar effect with CO₂ was suspected. The velocity and the absorption coefficient were measured at frequencies beginning in the dispersion region, theoretically and experimentally investigated by Kneser, and extending beyond it to 2.09 megacycles. The author's velocity values are slightly less than Kneser's experimental values but they fit his theoretically determined dispersion curve equally well. At the lowest frequency tested (303 kilocycles) the absorption coefficient was found to exceed, by the greatest amount, its value computed from Lebedew's formula. This frequency is near the middle of the dispersion region where maximum absorption is expected. According to Pierce the absorption becomes excessive also when this frequency is approached from lower values. The results are presented in tabular and in graphical form. A sharp absorption maximum appears at 217 k.c.

IF THE satellite spacing is used to compute the velocity of high-frequency sound in air as outlined in a previous article¹ the value $V_0 = 331.6$ m/sec. is obtained. If, however, the major peak spacing for short resonance columns is used the value of V_0 is usually about 0.5 percent higher than this, the excess being due, apparently, to the much greater intensity. A similar effect was suspected in the case of CO₂. It was, therefore, considered desirable to check the velocity measurements of H. O. Kneser² and to extend the region which he investigated, if possible. It was also considered desirable to search the dispersion region determined theoretically³ and experimentally by Kneser for excessive absorption.

The general method of investigation is the same as that used previously by the author¹ and by many other investigators. Some of the latest experimental investigations were reported by Barnes,⁴ Hershberger,⁵ Hopwood,⁶ Richards⁷ and Randall.⁸

APPARATUS

The apparatus is the same as that used in the previous investigation¹ with the addition of another thermometer mounted beside the sound path and a

¹ W. H. Pielemeier, *Phys. Rev.* **38**, 1236 (1931).

² H. O. Kneser, *Ann. d. Physik* [5] **11**, 777 (1931).

³ H. O. Kneser, *Ann. d. Physik* [5] **11**, 761 (1931).

⁴ G. F. Barnes, *J. Acous. Soc. Am.* **3**, 579 (1932).

⁵ W. D. Hershberger, *J. Acous. Soc. Am.* **3**, 263 (1931); also, *Physics* **2**, 269 (1932).

⁶ F. L. Hopwood, *Nature* **128**, 748 (1931).

⁷ W. T. Richards, *Proc. Nat. Acad. Sci.* **17**, 611 (1931); also, G. B. Kistiakowsky and W. T. Richards, *Jour. Am. Chem. Soc.* **52**, 4661 (1930).

⁸ C. R. Randall, *Bureau of Standards Jour. of Research* **8**, 79 (1932).

radiometer or pressure vane which could be interchanged with the moveable reflector. An orsat apparatus was used to analyze the gas after a run was completed.

RESULTS

The results are presented in Table I and in Figs. 1 and 2. The ratio, $V^2(\text{CO}_2)/V^2(\text{A})$, is plotted against $\log \nu$ in Fig. 1. In this figure $V(\text{CO}_2)$ represents the velocity of sound in CO_2 reduced to 0°C , the relative humidity ranging from 24 to 30 percent and the purity of the CO_2 ranging from 91 to 95 percent. $V(\text{A})$ represents the velocity in argon reduced to 0°C ($V(\text{A}) = 307.8$ m/sec.). This method of plotting is used in order to make a direct comparison with Kneser's² dispersion curve. The values of A , the absorption constant, are plotted against $\log \nu$ in Fig. 2. These values were computed from pressure vane deflections and also from the height of the peaks which were used for the velocity determinations.

TABLE I.

Frequency, in kilocycles	$V(\text{CO}_2)$ in meters per sec.	Percent CO_2	Relative humidity, H , in percent	$V^2(\text{CO}_2)/V^2(\text{A})$ in percent	c	$A = c\lambda^2$ $\times 10^{-3}$
303.8	262.5 to 265.1*	91 to 95	27 to 31	72.7 to 74.2	1.6	14.
409.6	264.3	94	—	73.7	1.7	8.1
645.8	265.1 to 267.0	91	24 to 30	74.2 to 75.3	1.7	3.2
1159.1	268.1 to 268.6	92 to 95	25 to 26	75.5	1.8	1.1
				75.7		
1224.	268.6 to 268.7	90	30	75.8	2.2	1.1
				75.9		
1403.	269.6 to 269.9	91 to 92	25 to 26	76.0	1.7	0.67
				76.2		
2089.	268.2	94	24	75.6	2.7	0.49

* The value from each of five runs was 263.6 (94 to 95 percent CO_2).

DISCUSSION OF RESULTS

With a resonance column of cross section small in comparison with the wave-length the wave fronts in the component trains rapidly lose their flatness and their intensity decreases much more rapidly than it would on account of mere absorption. If the cross section is kept constant and the frequency is increased this effect *diminishes* but the actual absorption *increases* in general. (Neglecting absorption *bands*, the coefficient of absorption should be porportional to the square of the frequency.) If the deviation from flatness is not prevented nor taken into account in absorption measurements an apparent or false absorption minimum might be found. With velocity depending on intensity such a minimum would be accompanied by an apparent dispersion. In consideration of these statements the measurements of Pierce,⁹ Barnes,⁴ and Kneser² on the velocity of high-frequency sound in CO_2 were viewed with a possible doubt and the upper range covered by Kneser was remeasured and extended to $\nu = 2089$ k.c. The coefficient of absorption was also measured over this range. Sound beams of greater cross section were

⁹ G. W. Pierce, Proc. Amer. Acad. **60**, 271 (1925).

used. The original intention was to use the satellites for the velocity determinations but they were so weak with CO₂ that this plan was rejected. Even with the lowest frequency ($\nu = 303.8$ k.c.) the satellites could be definitely located for only a few wave-lengths from the crystal surface. This fact and the constant space rate at which the logarithm of the peak height decreases

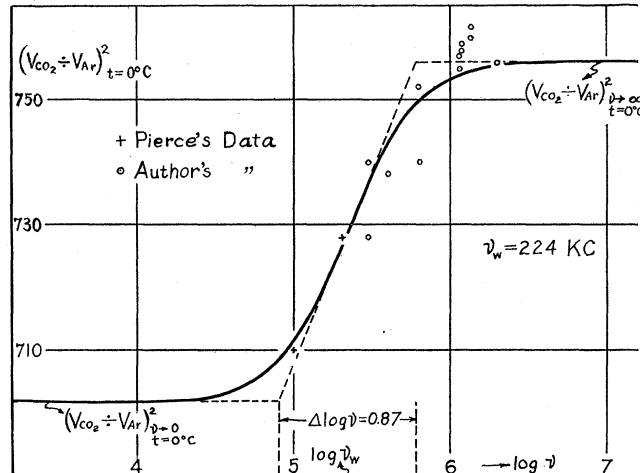


Fig. 1. Kneser's dispersion curve (ordinates $\times 10^{-3}$).

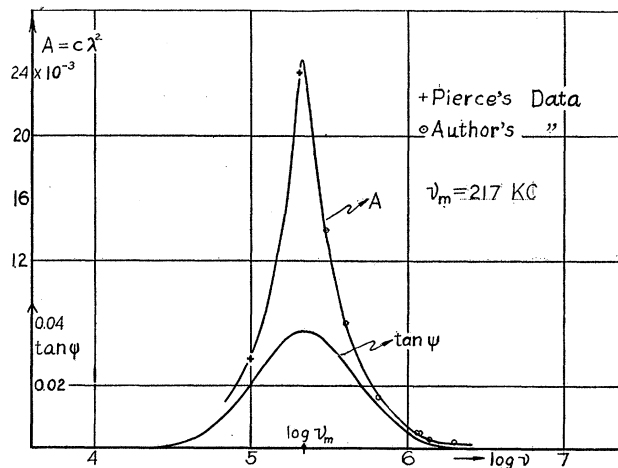


Fig. 2. Observed absorption curve and Kneser's $\tan \psi$ curve.

after the first few peaks, are good evidence that there is but one effective return trip of the emitted waves in CO₂.

Since the satellites observed with air at mirror positions such as to give resonance for low intensity (minimum velocity) waves could not be used with CO₂, the velocity values are probably slightly greater than the *limiting* velocity at the given frequency. The presence of some air (5 to 9 percent)

also has the effect of increasing the velocity. Probably the apparent drop in velocity between 1.4 and 2.09 megacycles is merely an approach to the limiting velocity for low intensity waves. (The intensity decreases through this range.)

A dispersion approximately as located by Kneser is quite evident in spite of the uncertainties listed above. Kneser's² observed maximum dispersion occurs at approximately 224 k.c. Pierce's⁹ velocity curve ends near this point (205.6 k.c.). It is in good agreement with Kneser's² curve. The author's data agree reasonably well with the remainder of Kneser's curve (see Fig. 1).

A number of different symbols for the absorption coefficient are used in the publications on sound absorption. Lebedew and Neklapajew¹⁰ use A/λ^2 , Abello¹¹ uses k for one percent CO_2 and therefore $100k$ for the pure gas, Herzfeld and Rice¹² use $4\pi k_2$ which they also express in terms of other constants including n^2 and τ , n being the frequency and τ a time measuring the rate of exchange between external and internal degrees of freedom. In Table I the symbol c is used for the absorption coefficient. ($I = I_0 e^{-cx}$). We may then write

$$100k = 4\pi k_2 = n^2 a = a/V^2 = c. \quad (1)$$

$$\text{From Eq. (1)} \quad a = A/\lambda^2 n^2 = A/V^2.$$

If there were no internal degrees of freedom nor dissociation of the molecules or if the internal energy were at all times in equilibrium with the external energy A and a would have constant values for all frequencies. This, however, is not the case with CO_2 . As may be seen from Table I, the greatest value of A observed by the author occurs with the lowest frequency (303.8 k.c.). Even this is above Kneser's² observed value for ν_w , the frequency for maximum dispersion, which is approximately 224 k.c. If that value of β is selected which yields 224 k.c. it is found to be $0.95(10)^{-6}$ and not $0.95(10)^{-5}$ sec. as he records it. This may be seen from Kneser's equation,

$$\nu_w = 224 \text{ k.c.} = 2.24(10)^5 = \frac{1}{2\pi} \frac{1}{\beta} \frac{C}{Ca} = \frac{1}{2\pi} \frac{1}{\beta} \frac{3.349}{2.5}.$$

Thus ν_m , the frequency for maximum value of ψ , has for its value 217 k.c. ψ represents the phase lag of the density behind the pressure. A *maximum* value of A is also expected at 217 k.c. Evidently A is approaching this maximum at the lower end of the observed frequency range. If the value of c at 303.8 k.c. is used to compute τ from the equation¹²

$$c = 4\pi k_2 = n^2 a = n^2 [3.16(10)^{-13} + 1.16(10)^{-4} \tau] \quad (2)$$

we obtain $\tau = 0.9(10)^{-7}$ sec.

This is not in agreement with Kneser's² *Abklingungszeit der inneren Energie* nor with β' , the life of the vibration quanta; *Lebensdauer der Schwingungs-*

¹⁰ N. Neklapajew, Ann. d. Physik **35**, 175 (1911).

¹¹ T. P. Abello, Phys. Rev. **31**, 1083 (1928).

¹² K. F. Herzfeld and F. O. Rice, Phys. Rev. **31**, 691 (1928).

quanten. $\beta' = (10 \pm 2)(10)^{-7}$ sec. The difference may be due to the values of c and n used in Eq. (2). With Abello's¹¹ interpolated value for 100 k , τ becomes $0.66 (10)^{-7}$ sec. This is for $n = 612$ k.c. which is farther above the peak frequency. Pierce⁹ states that 4 mm of CO₂ at 205.6 k.c. are more than equivalent to 204 mm of air. Accordingly τ is $3 (10)^{-7}$ sec. and $A = 24 (10)^{-3}$. If τ is computed from the first 2 mm of Pierce's⁹ curve the result is $8 (10)^{-7}$ sec. This frequency is just below that for the absorption peak. Probably τ for 217 k. c. would agree better with $\beta' = 10 (10)^{-7}$ sec. Peirce's⁹ data for 100 k.c. gives $5.7 (10)^{-3}$ as the value of A . This is definitely on the low-frequency side of the absorption maximum.

Small but very definite variations in the values of A for a given frequency were obtained by the author. These are probably due to the differences in the temperature and the humidity for the separate runs. This problem is being investigated and will be reported by H. H. Rogers.

Simultaneous measurements on velocity and absorption in other gases by a new method of detection¹³ are being investigated by H. L. Yeagley and H. L. Saxton.

Hershberger⁵ states two possible reasons for the multiple peaks which he observed. One is a frequency shift as the mirror approaches a resonance position. The other is the complexity in the motion of the crystal itself. The latter might well be the cause of those observed by the author. It is thought, however, that this complexity is *caused* by the slight deviation from simultaneity in arrival of the multiply reflected components of the stationary waves. Only the components of lowest intensity and minimum velocity arrive *together* if the length of the resonance column is adjusted for this minimum velocity.

¹³ In a recent article by Grossmann (Ann. d. Physik [5] **13**, 681 (1932)) a somewhat similar method is outlined. Grossmann's ν_m is lower and his maximum value of A is much greater than the author's corresponding values. The value of τ computed from Grossmann's maximum A is much in excess of $10(10)^{-7}$ sec. Possibly his method of correcting for diffraction is not sufficient to prevent an apparent additional absorption at the lower frequencies. If so, it would explain the above deviations. Further measurements near the peak frequency and below it are being made.