

The Specific heat of Carbon Dioxide and the form of the CO₂ molecule. By W. H. M^cCREA, B.A., Trinity College. (Communicated by Mr R. H. FOWLER.)

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Summary. Two alternative forms of the CO₂ molecule have been suggested by various authors who have discussed the band spectrum data. The specific heat curves based on these models are considered here. It is found that neither is quite satisfactory over the whole range of temperature and we discuss the difficulties for the low temperature and high temperature portions separately. In order to get agreement for low temperatures we find it necessary to introduce a further hypothesis about the molecular model which also seems to explain one or two outstanding difficulties in interpreting the fine structure of the bands. This assumption does not make any difference at higher temperatures where we show the error in one of the curves to be of the order we should expect to be accounted for by a centrifugal stretching of the molecule.

1. The evidence of the infra-red absorption bands of CO₂ on the form of the molecule has been considered by Bjerrum*, Dennison†, Schaefer and Philipps‡, and Eucken§. All except the last of these authors agree in assigning it the form of an isosceles triangle with the carbon nucleus at the vertex, as in Fig. 1 which shows the three normal modes of vibration which will be the three fundamental frequencies of the bands. The length of the arrows gives, roughly, the relative amplitude for each particle||.

If *A*, *B* and *C* are the principal moments of inertia of the system at its centre of gravity, the *C*-axis being parallel to *OO*, and the *B*-axis being the symmetry line, then *C* will be small compared with *A* and *B*, and, to a first approximation, *A* (= *B* + *C*) can be taken equal to *B*. Thus we have the case of a symmetrical rotator whose rotational energy levels will be¶

$$W_{j,n} = \frac{h^2}{8\pi^2} \left\{ j(j+1) \frac{1}{A} + n^2 \left(\frac{1}{C} - \frac{1}{A} \right) \right\} \dots\dots\dots(1),$$

* *Verh. d. D. phys. Ges.* xvi, p. 737 (1914).

† *Phil. Mag.* i, p. 195 (1926).

‡ *Zs. f. Phys.* 36, p. 641 (1926).

§ *Zs. f. Phys.* 37, p. 714 (1926).

|| Bjerrum (*l.c.*) obtains two solutions to the equations of motion—the present one and another—and he could not decide which should be taken.

¶ Dennison, *Nature*, Feb. 26, 1927, p. 316.

where $j = 0, 1, 2, \dots$ or $j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$
 $n = 0, \pm 1, \pm 2, \dots \pm j$, or $n = \pm \frac{1}{2}, \pm \frac{3}{2}, \dots \pm j$,

and, in the present case, $\frac{1}{C} \gg \frac{1}{A}$.

Using (1) the model predicts a fine structure for the bands in excellent general agreement with that observed, and gives

$$A \cong 50 \times 10^{-40} \text{ gm. cm.}^2,$$

$$C \cong 10^{-40} \text{ gm. cm.}^2,$$

assuming a gap of one line in the "n" series.

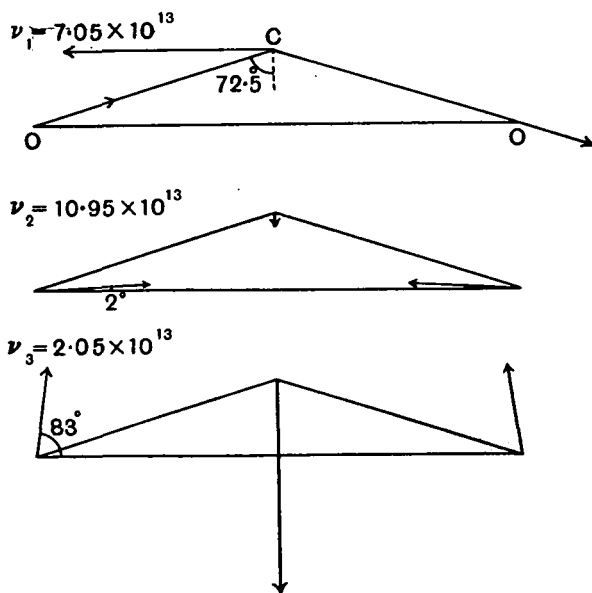


Fig. 1

Eucken, on the other hand, gives a model in which the three nuclei lie in a straight line with the carbon in the middle. His fundamental frequencies are

$$\nu_1' = 6.885 \times 10^{13} \text{ asymmetrical,}$$

$$\nu_2' = 3.670 \times 10^{13} \text{ symmetrical,}$$

$$\nu_3' = 2.019 \times 10^{13} \text{ perpendicular to the line of nuclei,}$$

and he assigns the fine structure to a departure of the vibrations from simple harmonic type.

We cannot here go into the details of the spectral evidence, which will be found in the papers quoted, for these two forms, except to say that, on the whole, it seems decidedly to favour the triangular type. It may be well, however, to mention one point noticed by Dennison, namely that, where a band is a double doublet, Eucken's explanation of the structure demands that half of it should be due to molecules excited one stage further than those molecules responsible for the other half in at least one fundamental frequency. This would predict a large difference of intensity instead of the more or less equal intensities actually observed.

2. We shall now consider the specific heat curves calculated on these two models. The former has one more rotational freedom and, giving the rotations their equipartition values, we obtain, in the usual manner, for the specific heat at constant volume,

$$\frac{C_v'}{R} = 3 + P\left(\frac{960}{T}\right) + P\left(\frac{3355}{T}\right) + P\left(\frac{5226}{T}\right) \dots\dots(2),$$

$$\frac{C_v''}{R} = \frac{5}{2} + 2P\left(\frac{960}{T}\right) + P\left(\frac{1750}{T}\right) + P\left(\frac{3287}{T}\right) \dots\dots(3),$$

for Dennison's and Eucken's models respectively. Here

$$P(x) = x^2 \frac{e^x}{(e^x - 1)^2},$$

and T is the absolute temperature in degrees Centigrade.

C_v' and C_v'' have been calculated for the range of temperature in which C_v has been measured and the results are given in the following table and the curves in Fig. 2.

The contribution of the ν_2 vibration to C_v' is only appreciable at high temperatures, but it is about twice the value of $C_v - C_v'$ at the end of the range.

One of Eucken's chief arguments for his model is that it does give a specific heat below $3R$ at low temperatures in agreement with experiment. We see, however, and this was not quite obvious from his paper since he was there concerned primarily with the low temperature behaviour, that (3) gives too large values at high temperatures. Now (2) and (3) both neglect the interaction of rotation and vibration, but we should expect a correction to be needed on this account, at such temperatures. This has been worked out for hydrogen* and increased the values calculated from a formula analogous to (2) and (3) and gave good agreement with experiment. We shall return to this below, but it is necessary to remark here that such a correction will presumably always increase the values derived from the crude formula, and, if so,

* Kemble and van Vleck, *Phys. Rev.* xxi, p. 653 (1923).

TABLE I.

<i>T</i> Absolute	<i>C_v'</i> Calculated from (2)	<i>C_v''</i> Calculated from (3)	<i>C_v</i> Observed	<i>C_v - C_v'</i>
155	6.12	5.28	5.02 ± 0.4	
197	6.33	5.72	5.83	
273	6.75	6.70	6.67	
373	7.17	7.76	7.14	
473	7.51	8.63	7.56	
573	7.83	9.32	7.96	
673	8.10	9.86	8.34	0.24
773	8.37	10.36	8.69	0.32
873	8.64	10.73	9.03	0.39
973	8.91	11.02	9.35	0.44
1073	9.15	11.25	9.65	0.50
1173	9.38	11.46	9.92	0.54
1273	9.60	11.63	10.18	0.58
1373	9.79	11.79	10.42	0.63
1473	9.99	11.93	10.63	0.64
1573	10.17	12.05	10.83	0.66
1673	10.33	12.16	11.00	0.67
1773	10.48	12.26	11.15	0.67
1873	10.59	12.33	11.29	0.70
1973	10.69	12.38	11.40	0.71
2073	10.77	12.43	11.49	0.72
2173	10.84	12.47	11.57	0.73
2273	10.90	12.50	11.62	0.72

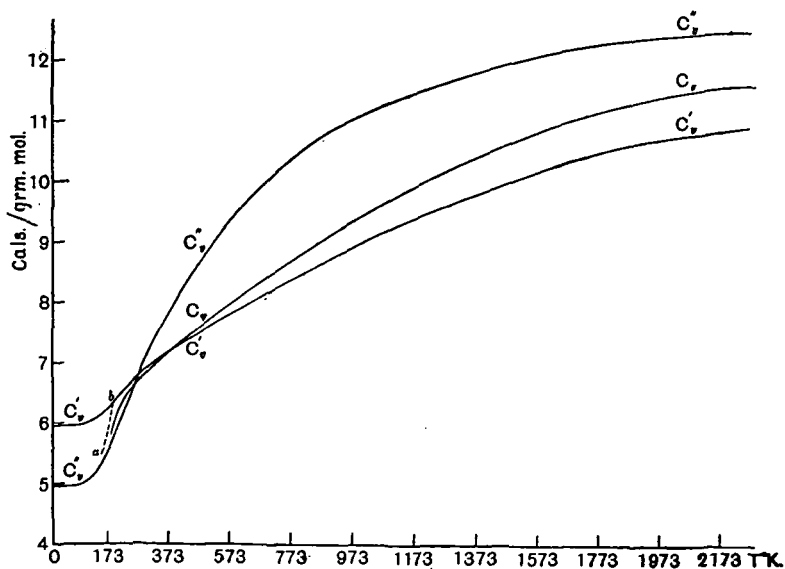


Fig. 2

any such formula predicting a value already too large must be impossible. Also, if there were a small amount of dissociation it would bring in a correction in the same direction. So it seems that Eucken's formula (3) cannot be accepted.

3. The next point is to consider whether Dennison's model will in any circumstances give values below $3R$. Now it is well known that in the case of hydrogen, on account of its small moment of inertia, the rotation does not reach its equipartition value until about 300° abs. and it was thought that here also the rotation about the small moment might show the same effect. To try this one proceeds as follows:

Equation (1) gives

$$\frac{W_{j,n}}{kT} = j(j+1)\sigma' + n^2\sigma \dots\dots\dots(4),$$

where $\sigma' = \frac{h^2}{8\pi^2 kT} \cdot \frac{1}{A}$, $\sigma = \frac{h^2}{8\pi^2 kT} \left(\frac{1}{C} - \frac{1}{A}\right)$ and $\sigma' \ll \sigma$.

The corresponding partition function is (j integral)

$$F(\sigma', \sigma) = \sum_{j=0}^{\infty} (2j+1) e^{-\sigma'j(j+1)} + 2 \sum_{j=1}^{\infty} \sum_{n=1}^j (2j+1) e^{-\sigma'j(j+1) - n^2\sigma} \dots\dots\dots(5),$$

taking the usual weight factors.

We shall suppose we are dealing with such values of T that σ' , but not σ , is very small (σ' will be small within a few degrees of absolute zero). It can be shown that*, for small σ' and $\alpha \ll \frac{1}{\sqrt{\sigma'}}$,

$$\sum_{j=\alpha}^{\infty} (2j+1) e^{-\sigma'j(j+1)} = \frac{1}{\sigma'} + O(1) \dots\dots\dots(6),$$

so that $F(\sigma', \sigma) = \frac{1}{\sigma'} \left[1 + 2 \sum_{n=1}^{\infty} e^{-n^2\sigma} \right] + O(1) \dots\dots\dots(7).$

The rotational specific heat, for small σ' , is therefore approximately

$$R \left\{ \sigma'^2 \frac{d^2}{d\sigma'^2} \log \frac{1}{\sigma'} + \sigma^2 \frac{d^2}{d\sigma^2} \log \left[1 + 2 \sum_{n=1}^{\infty} e^{-n^2\sigma} \right] \right\} \dots\dots(8).$$

The first term is just R , i.e. the equipartition rotation about the large moments, while the second, $R\sigma^2 \frac{d^2}{d\sigma^2} \log f(\sigma)$ (say), gives the contribution from rotation about the small moment. It is easily shown to tend to $\frac{1}{2}R$ as $\sigma \rightarrow 0$, as it must for equipartition.

* The second term on the R.H.S. is sometimes given as $O\left(\frac{1}{\sqrt{\sigma'}}\right)$, which is sufficient, but (6) is, in fact, true.

Values of this term have been calculated for different σ ; they give a curve rising very steeply to a maximum of something like \bar{R} and then approaching its asymptotic value of $\frac{1}{2}\bar{R}$ from above. To fit the observed values for $T=155^\circ$ and 197° on to the curve would require far too small a moment of inertia and the maximum would be quite contrary to the actual facts.

In some of the attempts to get a fit for hydrogen it was found better to omit the state of no rotation; so the effect of excluding all states for which $n=0$ was tried here, i.e. the first term (unity) was omitted from $f(\sigma)$. The resulting curve does not rise so steeply as the first. But even in this case C would have to be 0.14×10^{-40} gm. cm.² (approx.) to get agreement and we cannot reconcile this with the values from spectral evidence, especially since, if n can never be zero, the estimate of 10^{-40} above would have to be replaced by about 1.5×10^{-40} . Also the curve still possesses a maximum, though, indeed, it is now only about $0.56 \bar{R}$. Dennison (*Nature, l.c.*) has shown that half quantum numbers may be used in (1) even in the solution to the problem on the Wave Mechanics, so this was tried here. It did, indeed, give a curve rising asymptotically to $\frac{1}{2}\bar{R}$ without a maximum, but required C to be about 0.1×10^{-40} as against 10^{-40} from the spectrum. (Here

$$F(\sigma, \sigma') = 2 \sum_{j=\frac{1}{2}}^{\infty} \sum_{n=\frac{1}{2}}^j 2j e^{-\sigma'j(j+1) - n^2 \sigma^2}$$

leading finally to $f(\sigma) = \sum_{m=0}^{\infty} e^{-m(m+1)\sigma}$.

Lastly, in a strict application of the Wave Mechanics to the present case of a molecule which repeats itself for every half-revolution about the B -axis, the wave functions for the rotations divide into a symmetrical and an antisymmetrical series. There will be no intercombination between states belonging to different series, unless there is another wave function corresponding to some other property, say a nuclear spin, in which case the two sets of states may have different weights and we have to write*

$$F(\sigma, \sigma')$$

$$= \lambda \left\{ \sum_{j=0,2,4,\dots}^{\infty} (2j+1) e^{-j(j+1)\sigma} + \sum_{j=1,2,3,\dots}^{\infty} \sum_{n=1}^j (2j+1) e^{-j(j+1)\sigma - n^2 \sigma} \right\} \\ + (1-\lambda) \left\{ \sum_{j=1,3,5,\dots}^{\infty} (2j+1) e^{-j(j+1)\sigma} \right. \\ \left. + \sum_{j=1,2,3,\dots}^{\infty} \sum_{n=1}^j (2j+1) e^{-j(j+1)\sigma - n^2 \sigma} \right\} \dots (9),$$

where λ has some value between 0 and 1.

* The corresponding equation for a homopolar diatomic molecule is given by Hund, *Zs. f. Phys.* 42, p. 118 (1927).

It is seen, however, that the form when σ' is very small is exactly the same as (7)* for all λ , so that there is no change from the first case considered; and this is obviously true even if there is no intercombination, for each series gives by itself the same specific heat.

For half quantum numbers there is no change in the form of $F(\sigma, \sigma')$ when this division is taken into account.

4. The failure to get agreement with experiment in this manner for any probable value of the moment C , together with the success of this particular model in other directions, led one to look for other possible ways of accounting for this behaviour at low temperatures. The following hypothesis, which seems at first sight rather arbitrary, gives reasonably good agreement for the specific heat and also seems to account for some peculiarities, remarked by Dennison† in the fine structure of some bands.

We suppose that whenever the vibration ν_3 is not excited the molecule is linear, but that whenever it is excited the molecule has the triangular form we have been considering. Having made this assumption, it is natural to suppose that when the molecule is linear there will be no rotation about the line of nuclei, and that in the other form the state of no rotation about the corresponding (C) axis is excluded.

When the A and B rotations have their equipartition values, supposing that the ν_1 and ν_2 vibrations, which in any case make negligible contributions to the specific heat below about 300° abs., are independent (see below) of the suggested change of form, the partition function for the remaining rotation and vibration is

$$1 + 2 \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} e^{-m \frac{h\nu_3}{kT} - n^2 \sigma}$$

$$= 1 + \frac{2}{\left(e^{\frac{h\nu_3}{kT}} - 1 \right)} \left(\sum_{n=1}^{\infty} e^{-n^2 \sigma} \right) \dots\dots\dots(10).$$

This will, of course, give the usual values for high temperatures when the first term becomes unimportant.

Write $\frac{h\nu_3}{kT} = a\sigma$.

Then for $\nu_3 = 2.05 \times 10^{13}$ and $C = 1.01 \times 10^{-40}$,

$$a = 25,$$

* For example, $\sum_{j=0,2,4,\dots}^{\infty} (2j+1) e^{-j(j+1)\sigma'} = \frac{1}{2\sigma'} + O(1)$.

† *Zs. f. Phys.* 38, p. 137 (1926).

and it is found that (10) may be written without appreciable error as

$$1 + 2e^{-\alpha\sigma} \left(\sum_{n=1}^{\infty} e^{-n^2\sigma} \right) = \phi(\sigma) \text{ (say) } \dots\dots\dots(11).$$

This makes a contribution

$$R\sigma^2 \frac{d^2}{d\sigma^2} \log \phi(\sigma) \dots\dots\dots(12)$$

to the specific heat, which has been calculated for three temperatures, giving the results below which are indicated in Fig. 2 by the dotted curve *ab*.

TABLE II.

<i>T</i> Absolute	Calculated value of (12)	Resulting specific heat
158.4	0.237 <i>R</i>	5.44
180.0	0.430 <i>R</i>	5.82
198.0	0.628 <i>R</i>	6.32

ab is seen to lie quite reasonably near the experimental curve (the value $T = 155^\circ$, $C_v = 5.02 \pm 0.4$ is not shown in Fig. 2) and in obtaining this we have used a value of C (1.01×10^{-10}) of the order predicted by the optical evidence.

We may now consider briefly the optical behaviour of this molecule. Mechanically we do not expect the vibrations ν_1, ν_2 to be much affected by the contemplated change taking place in the form of the molecule, on account of the particular directions of vibration of the particles in the associated normal modes (Fig. 1) and the fact that the bending is really quite small. All we should anticipate is that ν_2 would become optically inactive in the linear form owing to the vanishing of the small vibration of the carbon nucleus.

In the ν_2 band the fine structure (Dennison, *Phil. Mag.*, *l.c.*) is due to switches $\Delta j = 0, \pm 1$; $\Delta n = \pm 1$ in $W_{j,n}$ given by (1), i.e. lines of spacing $\left(\frac{1}{C} - \frac{1}{A}\right) \frac{h}{4\pi^2}$ and $\frac{1}{A} \frac{h}{4\pi^2}$ superposed. What is actually observed is a double doublet formed of two lines of the first spacing, each of which becomes a Bjerrum doublet of unresolved lines of the second spacing.

On the simple theory we should expect the same structure for the ν_2 band, but it is observed only as a single doublet of separation similar to that of the above Bjerrum doublets. But, on our theory,

when ν_3 is absorbed by a switch from the straight form the C rotation is not initially excited, so that n must *increase*, and thus only half of the band formerly predicted is now possible. Also, if Δn must still be unity, the only possible switch for n is $0 \rightarrow 1$ and so only *one* line of the n series will be observed. The same will be true of the combination bands $\nu_1 + \nu_3$ and $3\nu_3$ observed by Schaefer and Philipps as single doublets*.

5. It remains to consider the magnitude of the discrepancy in C_v' at high temperatures. We saw that it was probably due to a centrifugal stretching of the molecule and we appealed to the analogous phenomenon in H_2 . In the diatomic case as treated by Kemble and van Vleck (*l.c.*) or Krätzer† the correction will be greater the

TABLE III.

T° Absolute	Hydrogen. Specific heat (vibration + rotation)			Difference		Carbon dioxide
	(i) Observed	(ii) Calculated by Kemble and van Vleck's method	(iii) Calculated by elementary theory $R + RP \left(\frac{6982}{T} \right)$	(i) — (iii)	(ii) — (iii)	$C_v - C_v'$ from Table I
673	2.12	2.08	2.01	0.11	0.07	0.24
1273	2.55	2.55	2.23	0.32	0.32	0.58
1873	3.11	3.36	2.66	0.45	0.70	0.70
2273	3.57	3.85	2.94	0.63	0.91	0.72

less the moment of inertia and the less the frequency of vibration. We notice now that in CO_2 in ν_3 , the *slowest* normal mode, the particles all vibrate in directions intersecting and almost perpendicular to the C -axis, the one about which the moment is *least*. Hence this combination of vibration and rotation will, presumably, be responsible for effectively the whole correction. Further C is greater than the moment of inertia of hydrogen‡ and ν_3 is less than its fundamental frequency‡ so a C , ν_3 dipole ought to have a

* Schaefer and Philipps remark that the band which they tabulate as $2\nu_2 - \nu_1$ may alternatively be given as $\nu_2 + 2\nu_3$. It is a double doublet and forms the only possible exception to what is said above.

On our theory the two lines of the n series in ν_2 , for example, will be due to switches in n of $1 \rightarrow 2$ and $2 \rightarrow 1$ (requiring again $C \cong 1.5 \times 10^{-40}$) and we still cannot explain why more lines of the series are not observed.

† See, for example, Born, *Atommechanik*, p. 140 *et seq.*

‡ For the values of these quantities see Kemble and van Vleck.

correction of the same order as H_2 . We estimate then that this combination in the triatomic molecule will give half the dipole value since the rotation has then, so to speak, only half the value. At any rate we are led to the conclusion that CO_2 should need a correction of the same order as H_2 . Table III shows that this is the case and that the error $C_v - C_v'$ exhibits the right kind of variation with temperature.

No way was found for working out for a triatomic molecule a complete theory similar to Kemble and van Vleck's. It would seem that, before working out the case of a non-rigid rotator, one would have to have an exact solution for a rigid rotator with unequal moments and it will be remembered that we have hitherto neglected the small difference between A and B . The latter problem has been worked out by Witmer* but is in itself so very complicated that it seems scarcely possible to apply additional corrections.

It was thought, therefore, that it might be worth while calculating the correction for a C, ν_3 dipole. Now the formula obtained by Kemble and van Vleck contains series which are really divergent, but from the physical nature of the problem we have only to take a certain number of the terms at the beginning. This presents no difficulty for the hydrogen case where the constants involved are such that the early parts of the series behave as though they were convergent. The constants for the C, ν_3 case, however, make the terms of some of the series increase from the start so that there is no way of knowing where to stop the series. Finally, one attempted to apply to the same dipole, Krätzer's formula, with what seemed possible values of the coefficients of the small correcting terms in the energy levels. Such a large number of terms had, however, to be taken that the working evidently was not sufficiently accurate, for the result was practically identical with that of the crude theory.

Thus the qualitative comparison with known results for Hydrogen already given seems the only method left to us for estimating the correction.

6. X-ray evidence shows the molecule of solid CO_2 to be linear and, since it seems certain that the gas molecule can have the triangular form, the transition from one form to another may take place in the manner we have suggested. There may be nothing in this argument if we consider the lattice structure of solids, but it seems natural that when the lattice breaks down into the separate molecules of the gas they should leave it with the straight form.

Lastly, if both forms are possible the presence of the straight molecules would reduce the average electric moment we should

* *Proc. Nat. Acad. Sci.* 12, p. 602 (1926). The method of the old Quantum theory is used but the new theory is bound to give a similar solution.

expect supposing they all had the bent form. Experiment does indicate a non-zero electric moment though its value is not definitely settled*.

In conclusion I wish to thank Mr R. H. Fowler, for suggesting the problem and for his invaluable advice.

* Zahn, *Phys. Rev.* 27, p. 455 (1926); Weigt, *Phys. Zs.* 22, p. 643 (1921); Jona, *Phys. Zs.* 20, p. 14 (1919).

[My attention has been called by Mr F. I. G. Rawlins to some work by Kliefoth, *Zs. f. Phys.* 39, p. 402 (1926), who obtains a non-zero moment agreeing with Weigt's but by a different method. (Added in proof.)]
