extension of the postulated mechanism in the absence of further experimental confirmation.

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[CONTRIBUTION FROM THE RADIOMETRY SECTION, ATOMIC AND RADIATION PHYSICS DIVISION, NATIONAL BUREAU OF STANDARDS]

The Structure of Ethylene from Infrared Spectra[1]

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From an analysis of the parallel band of C_2H_4 at 2988.66 cm.$^{-1}$ and the parallel band of C_2D_4 at 2201.013 cm.$^{-1}$ the inertial constants B and C for each molecule in the ground vibrational state were determined as $B = 0.9998$, $C = 0.8294$ and $B = 0.7334$, $C = 0.5636$, respectively. From these inertial constants the molecular parameters are deduced to be $r_{CC} = 1.337$ Å., $r_{CH} = 1.086$ Å. and $<_{HCH} = 177°22'$.

Introduction

Ethylene is one of the few relatively simple molecules for which there are still no adequate structural data. This molecule is very nearly a symmetric rotor, *i.e.*, the two large moments of inertia are nearly equal, and as a result previous studies[2,3] of the infrared spectrum have all been interpreted on a symmetric rotor model. The rotational Raman effect also has been observed,[4] but again the analysis was on the basis of a pseudo-symmetric rotor model.

In this type of analysis it is not possible to determine B and C directly but only $^1/_2\ (B + C)$. In order to make the separation of B and C, it is necessary to invoke the condition that $I_C = I_A + I_B$ which only holds for rigid planar bodies. This condition can introduce sizable errors into the structural parameters.

With the spectrometers available in this Laboratory it is possible to resolve the rotational fine structure due to the inequality of I_B and I_C and thus determine these parameters directly from the analysis of the data. This allows the determination of the structural parameters without assuming any relationship among the moments of inertia.

Experimental

The spectra were recorded with the grating instruments of the Radiometry Section[5] using a 10,000 line/in. grating with a ruled surface of about 6 by 8 inches. For the wave lengths shorter than 3.5 μ a cooled PbS cell was used as a detector while at longer wave lengths a cooled PbTe cell was used.

The band in both molecules was quite intense so could be observed at very low pressures. The C_2H_4 band was observed with pressures as low as 0.3 mm. of gas in a 1 m. cell while pressures as low as 1 mm. of C_2D_4 were used in the same cell. The wave lengths of the lines were measured by employing a Fabry–Perot interferometer as previously described.[6]

In the C_2H_4 band at 2988 cm.$^{-1}$, lines separated by 0.04 cm.$^{-1}$ were clearly resolved while in the C_2D_4 band at 2200 cm.$^{-1}$ the resolution was somewhat poorer, about 0.08 cm.$^{-1}$. Figures 1 and 2 are reproductions of recorder traces of the two bands made on white chart paper.

Analysis, C_2H_4

The C_2H_4 band near 2988 cm.$^{-1}$ is a parallel type band, *i.e.*, electric moment changes along the least inertial axis. The selection rules in the symmetric limit are $\Delta J = 0, \pm 1$, $\Delta K = 0$. In this limit the rotational levels for $K \neq 0$ are all doubly degenerate. If the inertial constants in the two vibrational states are nearly equal, then for each $\Delta J = \pm 1$ one would expect all the transitions for the various K to fall on top of each other giving rise to a series of equally spaced lines in the P and R branches. However, if $I_B \approx I_C$, the first-order perturbation causes a splitting of the $K = 1$ levels in each vibrational state. The selection rules for J remain the same, and likewise for K except that parity of asymmetric rotor wave functions must be considered leading to the selection rules[8] ee $\longleftrightarrow$ eo, oo $\longleftrightarrow$ oe. As a result for a given $\Delta J = \pm 1$, all the K transitions except those with $K = 1$ will fall on top of each other, and the two transitions with $K = 1$ will fall one on each side of the main grouping. Hence in this approximation, each P and R branch transition for a given J will appear as a triplet. As the quantity $B - C$ becomes large, higher order corrections to the energy enter and the splitting becomes more complex especially as J becomes higher. The simple triplet structure is clearly evident for P_2, P_3, R_1, R_2, R_3 in Fig. 1 although the splitting quickly becomes more complicated as J increases.

A set of C_2H_4 energy levels was calculated using Lord's[3] values for the inertial constants and published energy tables.[7]

From these energy values a trial spectrum was calculated using A-type selection rules,[8] (ee $\longleftrightarrow$ oe, oo $\longleftrightarrow$ eo) and relative intensities obtained by combining the line strengths[9] for $\kappa = -0.9$ with the appropriate Boltzmann and nuclear spin factors. For a planar model of C_2H_4 the nuclear

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[1] The work reported herein was supported by the U. S. Atomic Energy Commission.

[2] W. S. Gallaway and E. F. Barker, *J. Chem. Phys.*, **10**, 88 (1942).

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[8] P. C. Cross, R. M. Hainer and G. W. King, *ibid.*, **12**, 210 (1944).

[9] R. H. Schwendeman and V. W. Laurie, private communications.

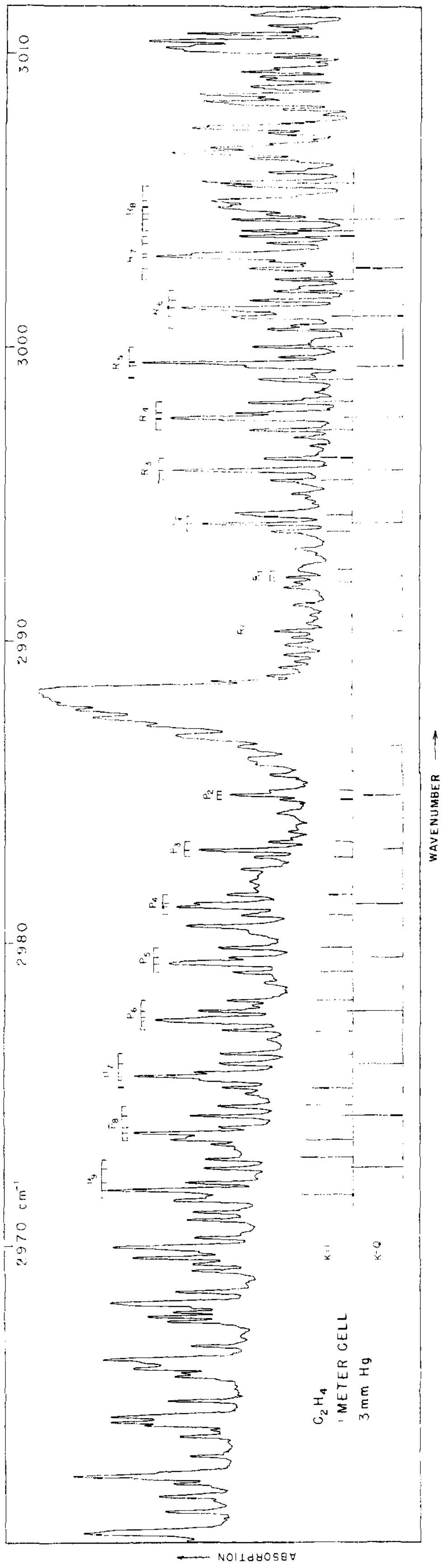

Fig. 1.—The parallel band of C_2H_4 at 2988.66 cm.$^{-1}$. The pressure was 0.3 mm. and the cell length was one meter.

spin statistics indicate there is a 7-fold degeneracy for the totally symmetric rotational states while rotational states of other symmetries have a 3-fold degeneracy arising from the 4 identical hydrogens. With the help of this trial spectrum specific assignments were made to many of the observed absorption peaks. Combination and difference values were obtained for both the ground and excited states from these assignments and final values of the inertial constants were obtained by solving about 30 equations of the type

$$\Delta F_{2\text{obsd}} - \Delta F_{2\text{calcd}} = \Delta\alpha a + \Delta\beta b + \Delta\gamma c$$

in which α, β and γ are the derivatives of the energy with respect to the inertial constants A, B and C.

There are certain limitations on the amount of information which can be obtained from a parallel type band of a nearly symmetric rotor. These can best be seen by consulting Table I which gives

Table I

Derivatives of Energy with Respect to Inertial Constants

$J_{K_{-1},K}$	α	β	γ
4_{40}	16.015	2.030	1.955
4_{41}	16.015	2.030	1.955
4_{31}	9.041	5.604	5.355
4_{32}	9.041	5.598	5.362
4_{22}	4.058	8.543	7.395
4_{23}	4.058	7.970	7.972
4_{13}	1.105	14.396	4.499
4_{14}	1.032	4.402	14.566
4_{04}	0.069	9.427	10.504
5_{50}	25.018	2.536	2.445
5_{51}	25.018	2.536	2.445
5_{41}	16.052	7.116	6.833
5_{42}	16.052	7.115	6.833
5_{32}	9.078	10.746	10.175
5_{33}	9.078	10.720	10.202
5_{23}	4.104	14.210	11.687
5_{24}	4.094	12.885	13.022
5_{14}	1.158	21.718	7.124
5_{15}	1.049	6.744	22.207
5_{05}	0.100	13.675	16.225

the derivatives of the energy with respect to the inertial parameters for $J = 4$ and 5. The derivative of the energy with respect to A, α, is essentially K^2 regardless of the J value. Since for this type band $\Delta K = 0$, the transitions have practically no dependence on the A inertial constant, hence A cannot be determined precisely from an analysis of an A-type band. However, the derivatives of the energy with respect to B and C (β and γ) vary considerably with J and K. In particular, the $K = 0$ and $K = 1$ transitions depend very strongly on B and C as can be seen from Table I. Since these are the transitions in which the splitting is the largest, these can be identified readily and make up the majority of the transitions used to form the differences used in the analysis. Thus excellent values of B and C can be obtained. From the convergence of the band, after B and C are determined for both vibrational states, it is also possible to determine the difference between the A constants in the two vibrational states. The band center is determined readily by adding or subtract-

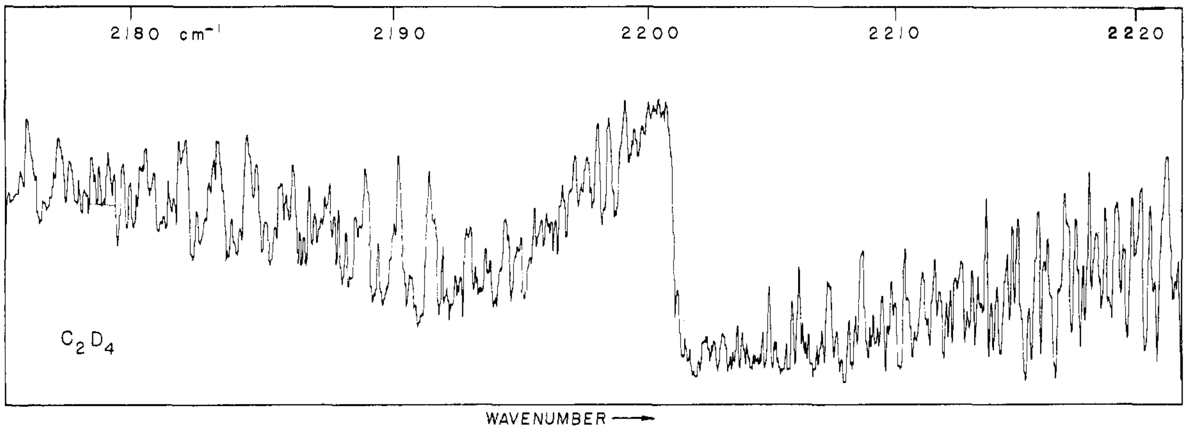

Fig. 2.—The parallel band of C_2D_4 at 2201.01 cm.⁻¹. The pressure of the gas was 1 mm. and cell length one meter.

ing the new calculated term values from the observed line positions and taking the average of these values. Using the band center and inertial constants deduced in this manner, it was possible to make 165 assignments in the P and R branches with $J \leqslant 10$ with an average deviation between the observed and calculated values of 0.04 cm.⁻¹. A comparison of the observed and calculated values for the $K = 0,1$ transitions is given in Table II. Since no J above 10 was used in the analysis, no centrifugal distortion correction was used. This will not introduce any appreciable error. In the symmetric limit the terms in the centrifugal distortion have the quantum number dependence $J^2(J+1)^2$, $J(J+1)K^2$, K^4. The coefficient of $J^2(J+1)^2$ is of the order of 10^{-6} so will not make any contribution to the energy, to the precision of this work until $[J(J+1)]^2 \sim 10^4$. The levels used to determine the inertial constants were those with $K = 0$ or 1, hence the contributions from the other two terms will also be negligible. Further, since it is the difference between the corrections which is of importance in the transitions, the error is further reduced. The values of the constants for this C_2H_4 band are

$\nu_0 = 2988.66$ cm.⁻¹ $B'' = 0.9998$ $C'' = 0.8294$
$\Delta A = -0.008$ $B' = 1.004$ $C' = 0.8237$

TABLE II

COMPARISON BETWEEN OBSERVED AND CALCULATED SPECTRUM

Transition	C_2H_4 Obsd.	C_2H_4 Calcd.	C_2D_4 Obsd.	C_2D_4 Calcd.
1_{01}–0_{00}	2990.50	2990.49	2202.308	2202.280
2_{02}–1_{01}	2992.30	2992.30	2203.529	2203.584
3_{03}–2_{02}	2994.12	2994.10	2204.815	2204.839
4_{04}–3_{03}	2995.76	2997.62		
5_{05}–4_{04}	2997.66	2997.62	2207.225	2207.224
6_{06}–5_{05}	2999.37	2999.32	2208.348	2208.338
7_{07}–6_{06}	3001.06	3001.03	2209.455	2209.464
8_{08}–7_{07}	3002.70	3002.68		
9_{09}–8_{08}	3004.34	3004.29	2211.632	2211.634
$10_{0,10}$–9_{09}	3005.95	3005.88		
2_{12}–1_{11}	2992.12	2992.12	2203.424	2203.433
3_{13}–2_{12}	2993.86	2993.84	2204.594	2204.611
4_{14}–3_{13}	2995.57	2995.46	2205.779	2205.795
5_{15}–4_{14}	2997.27	2997.25	2206.983	2206.967
6_{16}–5_{15}	2998.96	2998.93	2208.112	2208.133
7_{17}–6_{16}	3000.65	3000.59	2209.274	2209.266
8_{18}–7_{17}	3002.32	3002.24	2210.401	2210.399
9_{19}–8_{18}	3003.97	3003.88	2211.518	2211.518
$10_{1,10}$–9_{19}	3005.48	3005.49	2213.978	2213.974
2_{11}–1_{10}	2992.49	2992.49	2203.760	2203.758
3_{12}–2_{11}	2994.37	2994.41	2205.117	2205.125
4_{13}–3_{12}	2996.30	2996.32	2206.468	2206.475
5_{14}–4_{13}	2998.19	2998.24	2207.808	2207.808
6_{15}–5_{14}	3000.08	3000.14	2209.120	2209.116
7_{16}–6_{15}	3001.94	3002.03	2210.401	2210.391
8_{17}–7_{16}	3003.80	3003.91	2211.632	2211.629
9_{18}–8_{17}				
10_{19}–9_{18}	3007.51	3007.59		
0_{00}–1_{01}	2986.88	2986.83		
1_{01}–2_{02}	2985.01	2985.01		
2_{03}–3_{03}	2983.16	2983.19		
3_{03}–4_{04}	2981.38	2981.40	2195.948	2195.921
4_{04}–5_{05}	2979.60	2979.62		
5_{05}–6_{06}	2977.83	2977.87	2193.554	2193.545
6_{06}–7_{07}	2976.10	2976.14	2192.410	2192.392
7_{07}–8_{08}	2974.37	2974.42	2191.287	2191.250
8_{08}–9_{09}	2972.66	2972.72	2190.146	2190.107
9_{09}–$10_{0,10}$	2971.21	2971.17		
1_{11}–2_{12}	2985.16	2985.16		
2_{12}–3_{13}	2983.43	2983.40		
3_{13}–4_{14}	2981.67	2981.65		
4_{14}–5_{15}	2979.92	2979.90	2194.936	2194.950
5_{15}–6_{16}	2978.17	2978.14	2193.741	2193.756
6_{16}–7_{17}	2976.44	2976.38	2192.583	2192.568
7_{17}–8_{18}	2974.70	2974.62	2191.370	2191.383
8_{18}–9_{19}	2972.96	2972.86	2190.204	2190.204
9_{19}–$10_{1,10}$			2189.001	2189.031
1_{10}–2_{11}	2984.82	2984.83		
2_{11}–3_{12}	2982.92	2982.92		
3_{12}–4_{13}	2980.99	2981.03	2195.464	2195.472
4_{13}–5_{14}	2979.10	2979.14	2194.110	2194.112
5_{14}–6_{15}	2977.20	2977.27	2192.783	2192.768
6_{15}–7_{16}	2975.30	2975.41	2191.444	2191.448
7_{16}–8_{17}	2973.60	2973.57	2190.146	2190.160
8_{17}–9_{18}	2971.83	2971.74	2188.881	2188.911
9_{18}–10_{19}	2969.98	2969.94	2187.674	2181.702

It is interesting to note that the intensity distribution of the transitions originating in totally symmetric ground state levels clearly indicates that C_2H_4 is planar. This can be seen in Fig. 1 by considering the series of transitions there for which $K = 0$.

Analysis C_2D_4

The analysis of the C_2D_4 was complicated by the fact that the molecule is more asymmetric, causing considerable amounts of overlapping of the transitions originating in ground state levels of different J and also because the resolution is not quite as good as in the C_2H_4 band. The Q-branch is degraded to lower frequency and overlaps the low J transitions in the P-branch. For these reasons a slightly different method of analysis was used. A trial spectrum was calculated as in the case of C_2H_4 using the inertial constants deduced previously by Gallaway and Barker[2] as a starting point. For C_2D_4 the proper nuclear spin statistics are 27 for the totally symmetric rotational levels and 18 for the levels of other symmetry. This trial spectrum was compared to the observed absorption and adjustments were made in the calculated spectrum by means of the derivatives of the energy with respect to the inertial parameters in order to bring the two into closer agreement. Final adjustment of the constants was made by the solutions of 77 equations of the type

$$E_{\text{obsd}} - E_{\text{calcd}} = \Delta\nu_0 + \alpha'a' + \beta'b' + \gamma'c' - \alpha''a'' - \beta''b'' - \gamma''c''$$

by the method of least squares. The average deviation between observed and calculated values for the 77 transitions included in the least squares treatment was 0.01 cm.$^{-1}$. For about 130 transitions all with $J \leq 10$ the average deviation was about the same as in the C_2H_4 band. The values of the constants for this band are

$$\nu_0 = 2201.013 \qquad \Delta A = -0.014$$
$$B'' = 0.7334 \qquad C'' = 0.5636$$
$$B' = 0.7332 \qquad C' = 0.5636$$

The Structure of C_2H_4

In the usually assumed planar structure of C_2H_4 there are three independent structural parameters r_{CC}, r_{CH} and $<_{\text{HCH}}$. Since there are four inertial constants derived from the observed data, these three structural parameters are overdetermined. Fortunately the calculated structural parameters are independent of which three of the inertial parameters are used to calculate them. The structural parameters deduced from the ground state inertial parameters reported here are[10]

$$r_{\text{CC}} = 1.337 \text{ Å.} \qquad r_{\text{CH}} = 1.086 \text{ Å.} \qquad <_{\text{HCH}} = 117° 22'$$

The uncertainties in the inertial parameters given above are about 0.0002 cm.$^{-1}$ for C_2H_4 and somewhat larger for C_2D_4. The bond distances are relatively insensitive to small changes in the inertial constants; however, small changes in the inertial parameters can make considerable differences in the $<_{\text{HCH}}$. The uncertainty in the bond distances is of the order of 0.003 Å. while the uncertainty in the angle may be as much as a degree.

Discussion

The rotational constants of C_2H_4 agree fairly well with those determined previously from spectroscopic data.[2-4] However B is noticeably lower in the present work, which suggests that the effect of using the rigid body condition $I_C = I_A + I_B$ throws most of the defect, Δ, into this constant. It should be emphasized that this assumption has been eliminated from this work; however, only B_0 and C_0 have been used in calculating the molecular structure parameters and this procedure will introduce the errors inherent in using ground state inertial parameter in place of the equilibrium values. Since A was not determined there is no way to estimate the defect, Δ. The A constant can be determined from the analysis of a perpendicular band, but the structure of such a band is so complex that a real analysis was not possible with presently available resolution. The C–C distance in ethylene is shorter than the value obtained in reference 2. However, it does not seem out of line. If one assumes a linear relationship between bond order and C–C distance, then by using bond order $^3/_2$ and $r_{\text{CC}} = 1.397$ for benzene[11] and bond order 3 and $r_{\text{CC}} = 1.210$ for acetylene,[12] one calculates 1.334 Å. for C_2H_4 in excellent agreement with the observed value. The slightly smaller value $r_{\text{CC}} = 1.333$ Å. which recently has been determined for vinyl fluoride from microwave spectra[13] lends support to the value found here for C_2H_4.

The C–H distance is somewhat longer than the value of Gallaway and Barker[2] and about the same length as in benzene as might be expected.

This work shows that the HCH angle deviates considerably from the 120° previously reported. On the basis of the results for halogenated ethylenes this smaller angle again is to be expected.

The authors wish to thank Mr. E. D. Tidwell and Miss Jessie Kirkland for their help in recording and reducing the data.

WASHINGTON, D. C.

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(10) Since the preparation of this manuscript the structure of ethylene as determined by electron diffraction has been reported (L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **27**, 1414 (1957)). Their results, $r_{\text{CH}} = 1.085$ Å., $r_{\text{CC}} = 1.334$ Å., $<_{\text{HCH}} = 116°$, are in excellent agreement with those reported here.

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