TABLE II

SPIN-SPIN COUPLING CONSTANTS IN PERFLUOROALKYL DERIVATIVES OF SULFUR HEXAFLUORIDE[a]

Compound	$J_{CF_3-SF_4}$	$J_{CF_2-SF_4}$	$J_{CF_3C-SF_4}$	$J_{CF_3C-CF_2}$	$J_{CF_3CC-CF_2}$	$J_{CF_2-SF_a}$[b]	$J_{CF_2-SF_a}$[b]	$J_{SF_a-F_b}$[c]	$J_{CF_3-CF_2}$
$(CF_3CF_2)SF_4$		15.70	9.33						≦
$CF_3SF_4CF_2CF_3$	24.00	15.10	9.40						
$CF_3SF_4CF_2COOCH_3$	23.50	13.60							
$CF_3CF_2SF_5$		14.36	8.56			4.82		152.19	≦
$CF_3CF_2CF_2CF_2SF_5$[d]		17.0		10.80	2.42	4.93	2.47	145.96	≦
$CF_3SF_4CF_2SF_5$[e]	22.92	21.42				5.28		151.87	

[a] Coupling constants are given in units of cycles per second. [b] SF_a indicates the apex fluorine atom of the SF_5 group. [c] $J_{SF_a-F_b}$ is the coupling constant between the apex and base fluorine atoms in the SF_5 group. [d] $J_{CF_2-C-SF_4}$ must be about 8–9 c.p.s. in this compound to account for the SF_4 multiplet observed. Some assumptions concerning the relative magnitudes to be expected for certain of these coupling constants have been made in assigning them to particular pairs of groups. [e] $J_{SF_4-C-SF_4}$ must be about 10–12 c.p.s. in this compound to account for the SF_4 multiplet at −103.9 p.p.m. in Fig. 4.

three bonds, one would also expect the through-bond coupling in the F–C–C–F fragment to be appreciable. It has indeed been found[13] that *J trans* = 18.6 c.p.s. and *J gauche* = 16.2 c.p.s. for $CF_2Br-CFBr_2$ and, at least for the *trans* isomer, the through-space coupling should be small here. The hypothesis of Petrakis and Sederholm[12] that through-bond coupling is essentially zero for interaction *through* three single bonds therefore seems untenable and some other explanation of the low values for $J_{CF_3-CF_2}$ and $J_{CF_2-CF_2}$ must be sought. If the *trans* and *gauche* coupling constants were of opposite sign, then rotational averaging might indeed lead to the observed results. Unfortunately the only study of relative signs of F–F coupling constants which has been made[13] indicates that both *trans* and *gauche* coupling constants in $CF_2Br-CFBr_2$ have the same sign. Accidental mutual cancellation of through-bond and through-space interaction terms might also result in low *J* values but the problem remains a puzzling one.

Acknowledgments.—We are indebted to Professor J. A. Young and R. D. Dresdner of the University of Florida for the gift of these compounds and for much helpful discussion and to Dr. P. T. Narasimhan and Dr. J. C. Woodbrey for assistance in the preliminary stages of this work. The continued support of this research by the Atomic Energy Commission, through a grant, is gratefully acknowledged.

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(13) S. L. Manatt and D. D. Elleman, *J. Am. Chem. Soc.*, **84**, 1305 (1962).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN]

Hot Bands in the Infrared Spectra of Acetylenes in Solution

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The side band accompanying the acetylenic C–H stretching infrared band in solutions of acetylenes is shown to be a "hot band" absorption resulting from molecules in the first excited state with respect to the C–H bending mode. This appears to be the first reported observation of infrared hot bands in solution.

Splitting of the acetylenic carbon–hydrogen stretching band has been noted in recent infrared spectral studies of acetylenes.[1-3] A weak side band usually appears about 20 cm.$^{-1}$ lower in frequency than the main band. Previous workers have suggested that this vibrational doubling is due to Fermi resonance between the acetylenic C–H fundamental and a summation tone.[2,3] To investigate the nature of the side band more fully, we have investigated the spectral absorption of a number of acetylenes as a function of temperature, in the region of the C–H fundamental and first overtone.

Experimental

The methods of purification and preparation of the acetylenes and their physical constants have been described elsewhere.[4] Methylacetylene (Matheson Compressed Gases; 95% min. purity) was used without purification. Reagent grade carbon tetrachloride and 2,2,4-trimethylpentane from freshly opened bottles were used as solvents.

Infrared spectra in the C–H stretching region were determined with a Perkin-Elmer Model 112 spectrophotometer employing a lithium fluoride prism. The temperature of the 1 mm. cell employed was maintained to within ±0.5°. Slit widths were 0.085–0.10 mm. The same instrument, with a cesium bromide prism, was used for studies in the 400–700 cm.$^{-1}$ region. Spectra in the 5000–7000 cm.$^{-1}$ region were obtained with a Cary Model 14M Spectrophotometer equipped with thermostatted cell blocks. The temperature was constant to ± 0.1°. The path length used was 10 cm. and the slit widths were 0.2–0.32 mm. for slit heights of 20 mm. The scanning speed was 5Å./sec.

The values of n/n_0 used in the calculations are optical density ratios for the side band compared to the main band; The optical density of the side band was taken to be the maximum difference between the actual absorption curve and the approximated low frequency wing of the main band; the latter was obtained by reflection of the main band about its center. Ratios of n/n_0 for the spectra in the fundamental region are log I/I_0 values.

Discussion

A weak band is present approximately 20 cm.$^{-1}$ lower in frequency than the main acetylenic carbon–hydrogen stretching fundamental, in each of

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(1) R. A. Nyquist and W. J. Potts, *Spectrochim. Acta*, **16**, 419 (1960).

(2) J. C. D. Brand, G. Eglinton and J. F. Morman, *J. Chem. Soc.*, 2526 (1960).

(3) R. West and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **83**, 765 (1961).

(4) R. West and C. S. Kraihanzel, *Inorganic Chemistry*, **2**, in press.

TABLE I

POSITIONS OF FUNDAMENTALS AND HOT BANDS IN ACETYLENES IN CM.$^{-1}$

Compound	ν_{CH}	$\nu_{CH}+\nu_i-\nu_i$	$2\nu_{CH}$	$2\nu_{CH}+\nu_i-\nu_i$	Concn., *M* at 25°	Temp. range, °C. (no. of meas.)	Avg. ν_i calcd,	δ_{CH} obsd.
$CH_3C{\equiv}CH$	3316	3298	6530	6429	*ca.* 0.1	19.9–55.1 (5)	665	630
n-$C_4H_9C{\equiv}CH$	3314	3296	6525	6486	.056	20.8–49.7 (5)	650	627
n-$C_5H_{11}C{\equiv}CH$	3314	3295	6525	6486	.052	19.8–68.3 (5)	655	(627)
n-$C_5H_{11}C{\equiv}CH$[a]	[d]	[d]	6537	6497	.041	19.8–57.4 (4)	650	(627)
n-$C_6H_{13}C{\equiv}CH$	3314	3295	6527	6488	.040	19.5–69.0 (7)	660	(627)
n-$C_6H_{13}C{\equiv}CH$	3314	3295	6527	6488	.06	26.5 and 66.0[c]	665[c]	630
n-$C_6H_{13}C{\equiv}CD$	2599	2585	5158	5126	.124	20.2–60.8 (5)	535	492
n-$C_6H_{13}C{\equiv}CD$	2599	2585	5158	5126	*ca.* .15	28.5 and 66.5[c]	560[c]	492
$Me_3SiC{\equiv}CH$	3293	3278	6482	6445	.090	−1.4–39.6 (5)	690	672 or 651
$Ph_3SiC{\equiv}CH$	3293	3278	6480	6444	.058	20.1–67.6 (5)	695	[d]
$Ph_3SiC{\equiv}CH$	3293	3278	6480	6444	.06	28.0 and 70.0[c]	675[c]	[d]
$EtSC{\equiv}CH$	3308	3289	6512	6473	*ca.* .03	20.0–59.0 (5)	605	669

[a] In 2,2,4-trimethylpentane. [b] From measurements in the first overtone region except where noted. [c] Measurements in the fundamental region. [d] Not measurable because of interferences.

the monosubstituted acetylenes which were studied (Table I). The splitting is about 40 cm.$^{-1}$ in the first overtone region. Nyquist and Potts consider the possibility that the side band represents a summation of the first overtone of the acetylenic C–H deformation mode (1250 cm.$^{-1}$) with the C≡C stretching mode (2120 cm.$^{-1}$); the observed intensity would then be the result of Fermi resonance with the carbon-hydrogen stretching mode.[2] We have previously noted that the C–D stretching absorption in deuterated acetylenes has a similar split pattern.[4] This observation makes Fermi resonance seem an unlikely explanation for the side band, since an entirely different summation would have to be involved in the deuterated compounds.

The side band cannot be attributed to rotation-vibration interaction because molecular rotation should be effectively prevented in solution. Intermolecular hydrogen bonding cannot be responsible for the side band, because the band persists at low concentrations where self-association of acetylenes by hydrogen bonding is known to be negligible.[4] Furthermore, the intensity of the side band *increases* with increasing temperature (Fig. 1), whereas the opposite would be true of hydrogen-bonded C–H bands.

The effect of temperature on the intensity of the side band leads to what we believe to be the correct explanation for this absorption. Similar temperature-dependent side bands, called "hot bands," have often been observed in the infrared spectra of gases.[5] The hot band represents the same spectral transition as the fundamental with which it is associated except that the hot band transition occurs only for molecules which are in a low-lying energy level above the ground state. The distribution of molecules between the ground state and this particular excited state is given by the Boltzmann equation, where n is the relative number of molecules in an energy state E of degeneracy g above the ground state, at temperature T

$$\frac{n}{n_0} = \frac{g}{g_0}e^{-E/kT} = \frac{g}{g_0}e^{-h\tilde{\nu}_i c/kT}$$

n_0 and g_0 refer to the ground state. The ratio of the numbers of molecules in the two states, n/n_0, may be taken to be equal to the ratio of the absorbancies of the fundamental and the associated hot band if the probabilities of the two transitions are assumed to be nearly equal. By choosing proper degeneracy values, the energy level E or the frequency ν_i of the corresponding normal mode of the molecule may be determined.

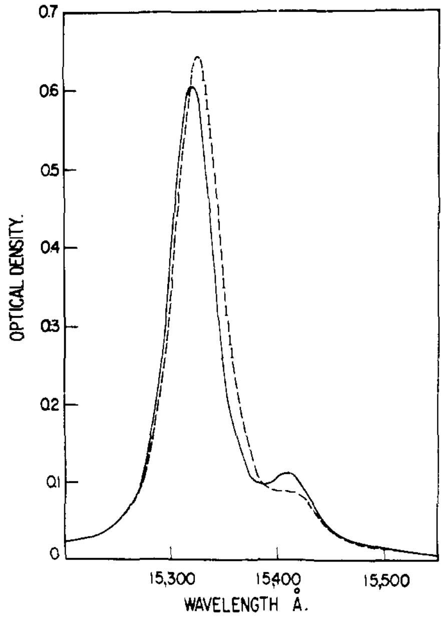

Fig. 1.—The first overtone of the —C—H stretching absorption of 1-heptyne, 0.040 *M* in CCl_4; dashed line, 19.5°; solid line, 69.0°.

The hot bands observed in the spectra of acetylenes in solution will be discussed with the aid of the partial energy level diagram in Fig. 2, for molecules of C_{3v} symmetry. The ground state is non-degenerate. The energy level in which the excited molecules reside will correspond to a low energy deformation band (ν_i). For acetylenes $R_3E—C{\equiv}C—H$, of C_{3v} symmetry, the E—C≡C and C≡C—H deformation modes, which are both doubly degenerate, are of a suitable energy to give rise to hot bands. Absorption of radiation corresponding to the acetylenic carbon–hydrogen stretch (ν_k) gives rise to molecules in the levels ν_k and ν_k

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(5) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1945, pp. 266–269, 389–392.

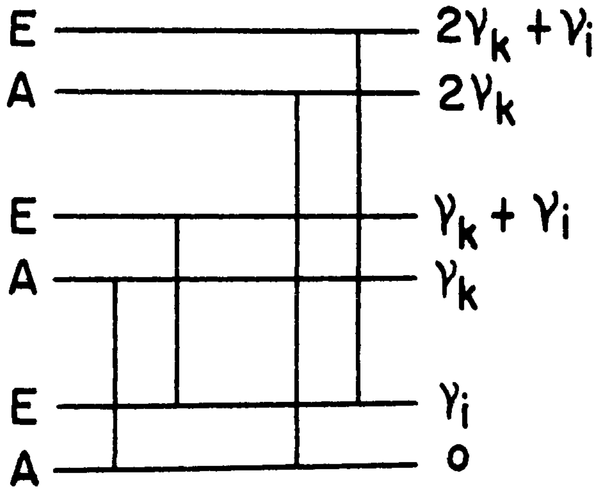

Fig. 2.—Simplified energy level diagram for acetylenes of C_{3v} symmetry.

$+ \nu_i$; the transitions are ν_k and $\nu_k + \nu_i - \nu_i$. The level $\nu_k + \nu_i$ must also be doubly degenerate. Similarly, the transitions $2\nu_k$ and $2\nu_k + \nu_i - \nu_i$ may occurr and will give rise to hot bands associated with the first overtone of ν_k.

The identical degeneracies for the two low frequency bending modes of monosubstituted acetylenes of symmetry C_{3v} permit a clear distinction between the two possibilities for ν_i. In Table I are given some observed values for ν_i obtained from near infrared spectra for methylacetylene, trimethylsilylacetylene and triphenylsilylacetylene. The agreement of calculated values over the temperature range studied for each acetylene is excellent. These results indicate that the hot band is arising from molecules in the energy level ν_i corresponding to the acetylenic carbon–hydrogen deformation band, which occurs near 650 cm.$^{-1}$. The alternate (E—C≡C) deformation mode occurs near 350 cm.$^{-1}$ in 1-propyne and at even lower frequencies in silylacetylenes.[6]

Although 1-hexyne, 1-heptyne and 1-octyne are of lower symmetry, the near degeneracy of the carbon–hydrogen bending mode is attested to by the fact that only one band is observed in the 630 cm.$^{-1}$ region. Calculations on these 1-alkynes employing a degeneracy ratio of two to one also lead to a frequency of about 650 cm.$^{-1}$ for ν_i, supporting the argument given above. Still further support is obtained from studies with 1-octyne-d_1. The temperature variation in this deuterated acetylene leads to a frequency for ν_i of about 530 cm.$^{-1}$. The C–D bending mode occurs near 500 cm.$^{-1}$.[7] Similar studies of temperature dependence were carried out for a few of the compounds in the fundamental region (Table I). Although the results are less accurate, they lead to approximately the same frequencies for ν_i.

All of the evidence is thus consistent with the assignment of the side bands as hot bands resulting from molecules in the first excited state with respect to δ_{CH}, the acetylenic C–H deformation mode. If the fundamental and first overtone are designated as ν_{CH} and $2\nu_{CH}$, their associated hot bands should be designated as $\nu_{CH} + \delta_{CH} - \delta_{CH}$ and $2\nu_{CH} + \delta_{CH} - \delta_{CH}$, respectively. The results, both in the fundamental and first overtone region, lead to a value of about -20 cm.$^{-1}$ for the anharmonicity constant x relating the two modes. Such constants are normally much smaller for large molecules. The unusually large anharmonicity indicates that ν_{CH} and δ_{CH} interact strongly and probably are largely decoupled from the rest of the vibrations in the molecule.

A series of hot bands corresponding to these have been observed in the spectra of gaseous acetylene. The relevant anharmonicity constant in acetylene, x_{14}, is -16.46 cm.$^{-1}$.[8] Quite different hot bands associated with ν_{CH} have also been observed previously in the gas spectra of methylacetylene and its deuterated derivatives.[7–10] These hot bands result from excitation with respect to the methyl deformation; the anharmonicity is much smaller (1–2 cm.$^{-1}$). Similar excitation undoubtedly takes place in solution, but the resulting hot bands are not resolved from the broad C–H fundamental. The previous workers did not notice the widely-split hot band due to the 650 cm.$^{-1}$ energy level in the spectrum of gaseous methylacetylene, perhaps because its absorption is thinly spread over the complicated rotation-vibration fine structure.

So far as the authors are aware, the bands described above are the first reported examples of hot bands observed in the infrared spectra of liquids or solutions. However, it does not seem that the large anharmonicity observed in substituted acetylenes should be unique, and with increasing use of infrared spectrometers with moderately high resolving power it seems likely that other examples of hot bands observable in solution will be discovered.[11] When possible it may prove quite convenient to study such hot bands in solution because interference due to rotational levels will thereby be eliminated.

ADDED IN PROOF.—A recent communication reports independent observation of the $\nu_{CH} + \delta_{CH} - \delta_{CH}$ hot band in 1-heptyne [Phan Van Huong and Jean Lascombe, *Comp. Rend.*, **254**, 2543 (1962)].

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(6) H. Büchert and W. Zeil, *Z. physik. Chem.* (Frankfurt), **29**, 317 (1961).

(7) R. J. Grisenthwaite and H. W. Thompson, *Trans. Faraday Soc.*, **50**, 212 (1954).

(8) H. C. Allen, Jr., E. D. Tidwell and E. K. Plyler, *J. Research Natl Bur. Standards*, **57**, 213 (1956).

(9) G. Herzberg, F. Patat and H. Verleger, *J. Phys. Chem.*, **41**, 123 (1937).

(10) D. R. J. Boyd and H. W. Thompson, *Trans. Faraday Soc.*, **48**, 493 (1952); *ibid.*, **49**, 141 (1953); M. L. Christensen and H. W. Thompson, *ibid.*, **52**, 1439 (1956).

(11) An example has already come to the authors' attention through private communication with Prof. T. L. Brown, who reports observation of probable hot bands in the infrared spectrum of *p*-benzoquinone (T. L. Brown, *Spectrochim. Acta*, **18**, in press.)