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### Title

PRESSURE BROADENING OF SINGLE VIBRATIONAL-ROTATIONAL TRANSITIONS OF ACETYLENE AT  $v = 5$

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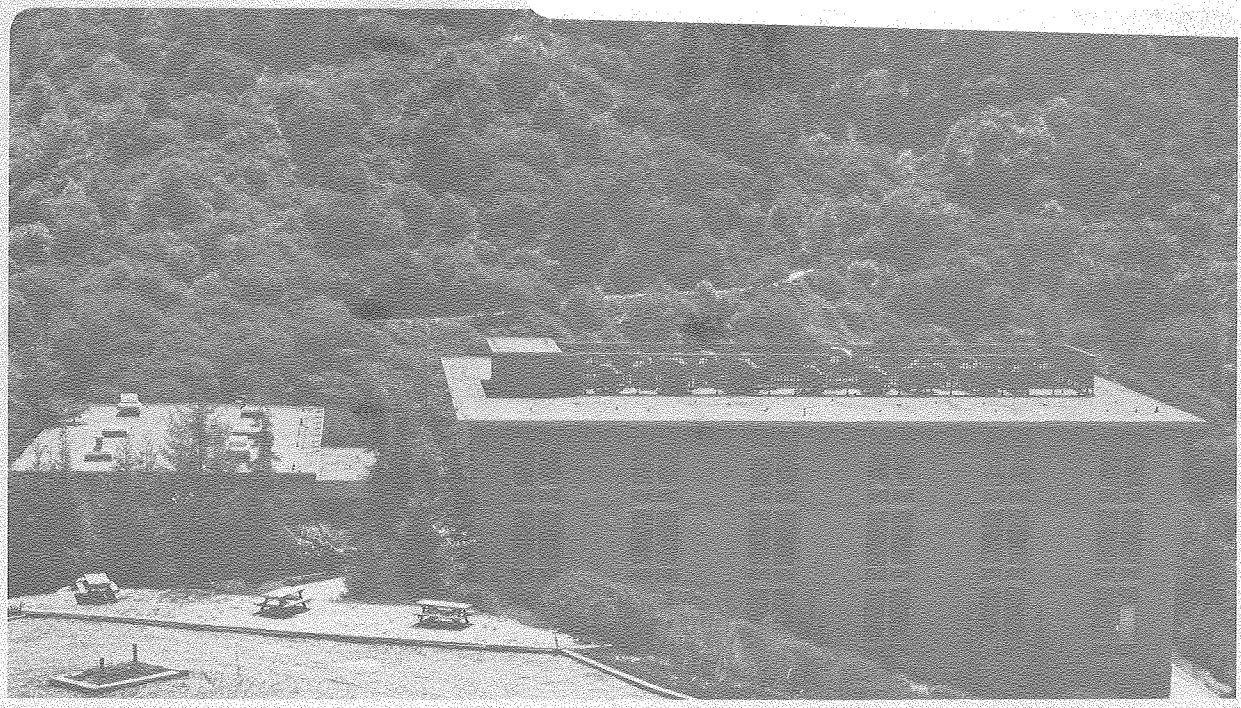
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James S. Wong

February 1980

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PRESSURE BROADENING OF SINGLE VIBRATIONAL-ROTATIONAL  
TRANSITIONS OF ACETYLENE AT  $v = 5$

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7 pages

1 figure

1 table



PRESSURE BROADENING OF  $C_2H_2$

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PRESSURE BROADENING OF  $C_2H_2$

LIST OF SYMBOLS

$\nu$       Nu

$\gamma$       Gamma





PRESSURE BROADENING OF SINGLE VIBRATIONAL-ROTATIONAL  
TRANSITIONS OF ACETYLENE AT  $v = 5$

To understand the mechanism of pressure broadening one must have accurate values of the pressure broadening coefficients as a function of vibrational quantum number. Unfortunately, such data for polyatomic molecules are scarce. The coefficient for self-broadening of methane has been found to be the same for the R(0) and R(1) lines of the  $2\nu_3$  and  $3\nu_3$  bands and for an unidentified line of the  $5\nu_1 + \nu_3$  band at  $6190 \text{ \AA}$  (1). Measurements have also been performed on the  $\nu_2$  (2) and  $\nu_1 + \nu_3$  (3) bands of acetylene. In the work described here, high resolution spectra of single vibrational-rotational lines of the  $5\nu_3$  band of acetylene at  $15\,600 \text{ cm}^{-1}$  have been taken to determine the coefficients for self-broadening at a much higher level of vibrational excitation.

A single frequency cw dye laser (Spectra-Physics 580A) with Rhodamine B as the lasing medium is used as a narrow bandwidth light source. The laser is continuously scannable over a 10 GHz region with 30 MHz linewidth. The unfocused beam is chopped and directed through a small, nonresonant optoacoustic cell (4). The pressure of the acetylene (> 99.99% purity) in the cell is measured with a capacitance manometer. The optoacoustic signal is detected by a miniature electret microphone placed within the cell and is processed by a lock-in amplifier. The high resolution scans are calibrated ( $\pm 5\%$ ) by monitoring the dye laser output with a spectrum analyzer



equipped with 2 GHz FSR mirrors. All spectra were taken at room temperature ( $293 \pm 2$  K).

At the relatively low pressures used in these experiments, the experimental linewidths are not more than three times the Doppler width (1.1 GHz FWHM). The method of Gronwall (5) was used to calculate values of the Voigt lineshape. With these data, the pressure broadened widths,  $\Delta\nu_p$ , were extracted from the experimental lineshapes and are plotted as a function of pressure for the R(3), R(9), and R(15) lines in Fig. 1. The lines drawn through the data points were determined by the linear least squares method. The self-broadening coefficients,  $\gamma$ , and their standard errors are summarized in Table I along with the results of other workers.

The values of  $\gamma$  obtained for the  $5\nu_3$  rotational lines agree with those of  $\nu_1 + \nu_3$  (3), within the experimental errors. When comparing the results of Fabelinsky et al. (2), it must be noted that their broadening coefficient was obtained by plotting the observed linewidths vs pressure for pressures less than 0.5 atm. Since no corrections were made for the coexistence of Doppler and pressure broadening, the actual value of  $\gamma$  is somewhat larger than that reported. Thus within the experimental uncertainties, the coefficient for self-broadening is independent of vibrational excitation over a range of 2 000 to 15 600  $\text{cm}^{-1}$ . To test the theories of Giraud et al. (6) and Green (7) discussing the vibrational dependence of pressure broadening, one would have to determine  $\gamma$  quite accurately to resolve any subtle changes that may exist.



Acetylene is an excellent polyatomic molecule for a detailed experimental study since the rotational structure of the overtone spectra is readily resolved and the absorption cross sections of single rotational lines are large.

#### ACKNOWLEDGMENTS

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REFERENCES

- (1) J. Gelfand, W. Hermina, and W.H. Smith, Chem. Phys. Lett. 65, 201-205 (1979).
- (2) V.I. Fabelinsky, B.B. Krynetsky, L.A. Kulevsky, V.A. Mishin, A.M. Prokhorov, A.D. Savel'ev, and V.V. Smirnov, Opt. Commun. 20, 389-391 (1977).
- (3) P. Varanasi and B.R.P. Bangaru, J. Quant. Spectrosc. Radiat. Transfer 15, 267-273 (1975).
- (4) C.F. Dewey, Optoacoustic Spectroscopy and Detection, Y.H. Pao, ed., Chapter 3, Academic Press, New York, 1977.
- (5) S.S. Penner, Quantitative Molecular Spectroscopy and Gas Emissivities, 51-53, Addison-Wesley, Reading, MA, 1959.
- (6) M. Giraud, D. Robert, and L. Galatry, J. Chem. Phys. 59, 2204-2214 (1973).
- (7) S. Green, J. Chem. Phys. 70, 4686-4693 (1979).





TABLE I

Self-broadening coefficients of acetylene at room temperature

Vibrational Band	Rotational Line	Energy ( $\text{cm}^{-1}$ )	Reference	$\gamma$ (MHz torr $^{-1}$ )
$5\nu_3$	R(3)			12.1 $\pm$ 0.3
	R(9)	15 600	This work	9.89 $\pm$ 0.46
	R(15)			8.48 $\pm$ 0.76
$\nu_1 + \nu_3$	R(5)			10.7 <sup>b</sup>
	R(7)			9.8 $\pm$ 0.2
	R(9)			10.2 $\pm$ 0.2
	R(11)			10.1 $\pm$ 0.2
	R(13)			9.5 $\pm$ 0.3
	R(15)	6 560	(3)	9.8 $\pm$ 0.2
	R(17)			7.7 $\pm$ 0.3
	R(19)			7.1 $\pm$ 0.6
	R(21)			7.5 $\pm$ 0.7
$\nu_2$	Q branch	1 972	(2)	8.3 <sup>a,b</sup>

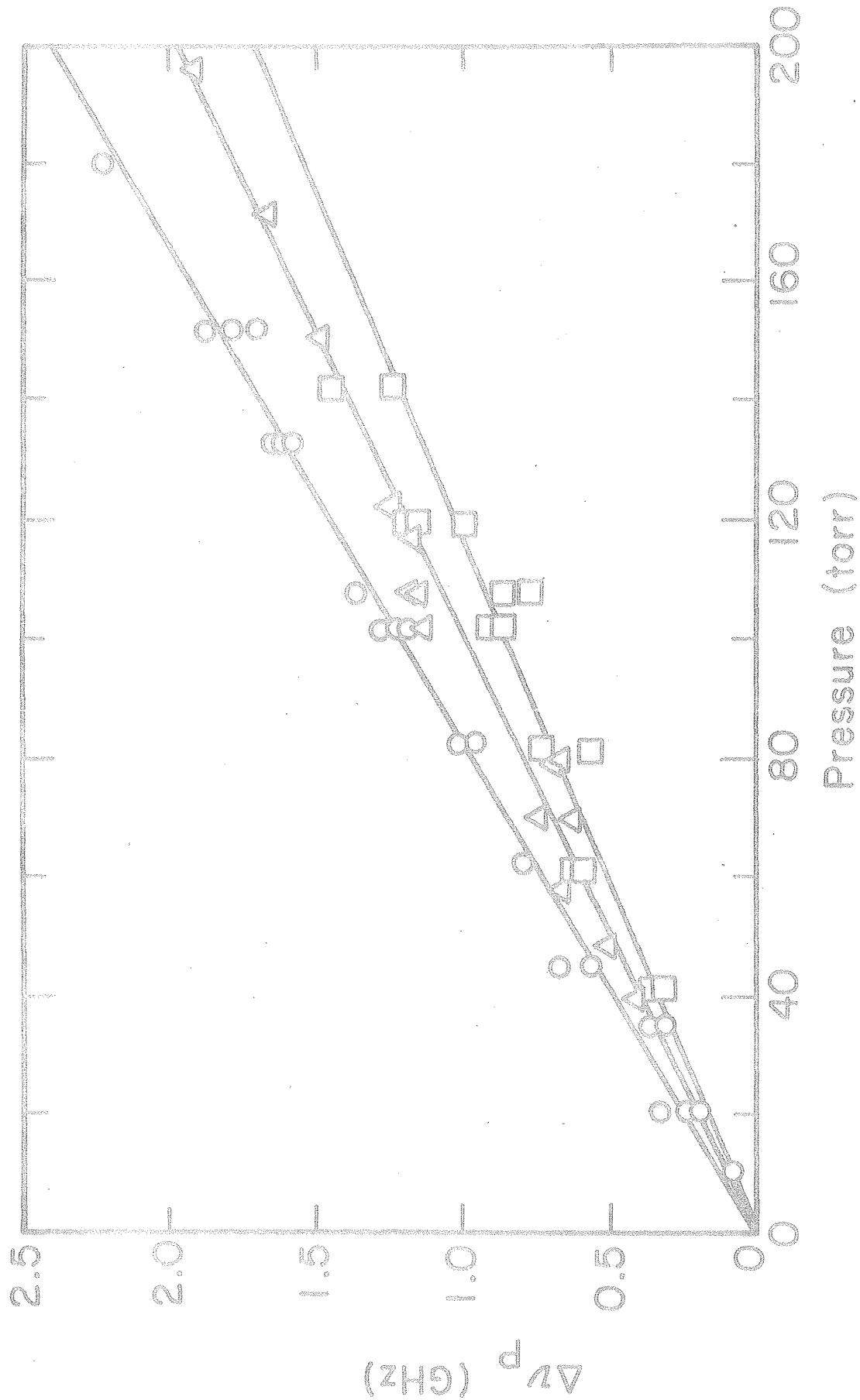
<sup>a</sup>See text.<sup>b</sup>No uncertainties were given.



FIGURE CAPTION

Figure 1. Room temperature self-broadened widths,  $\Delta\nu_p$ , vs pressure for the R(3) (O), R(9) ( $\Delta$ ) and R(15) ( $\square$ ) rotational lines, respectively, of the  $5\nu_3$  band of acetylene.





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FIG. 1

