

Raman Effect in Liquid Acetylene

George Glockler and Malcolm M. Renfrew

Citation: [The Journal of Chemical Physics](#) **6**, 340 (1938); doi: 10.1063/1.1750264

View online: <http://dx.doi.org/10.1063/1.1750264>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/6/6?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Raman Spectra of Acetylenes IV. Carbon Isotope Effect in Acetylenes](#)

J. Chem. Phys. **9**, 390 (1941); 10.1063/1.1750920

[Raman Effect in Liquid Ethane](#)

J. Chem. Phys. **6**, 295 (1938); 10.1063/1.1750247

[Raman Effect in Liquid Ethylene](#)

J. Chem. Phys. **6**, 170 (1938); 10.1063/1.1750221

[Raman Effect of Acetylenes II. Diiodoacetylene, Liquid Acetylene and Deuteroacetylenes](#)

J. Chem. Phys. **4**, 15 (1936); 10.1063/1.1749740

[Raman Effect of Acetylenes. I. Methyl, Dimethyl and VinylAcetylene](#)

J. Chem. Phys. **2**, 881 (1934); 10.1063/1.1749411



$c' < 0$ and $2c - c' > 0$. This is obviously $S_{12} = S_{34} = 0$ and $|S| = 1 - |y|$ and the equilibrium energy at absolute zero has the form

$$E = N[4(2c - c')|y| + 4c'y^2],$$

which is plotted in Fig. 1. A well-known property of these curves is that if a common tangent can be drawn to two points on the curve, and the tangent is everywhere below the curve, then an alloy having a composition represented by a point between the points of tangency, as for instance point 0 on the figure, will break up into two phases having the compositions 1 and 2. For $c > 0$, therefore, we shall have either pure A or pure B in equilibrium with a perfectly ordered compound AB at the absolute zero. For $c < 0$ any alloy will break up into pure A and pure B, but as the temperature is raised it may happen that the intermetallic compound AB will be formed. The precise manner in which the compound and the degree of order will be influenced by the temperature will depend on the relative magnitude of the constants c and c' .

Even after including the next nearest neighbor interaction, the phase diagrams will be symmetrical in A and B, as was pointed out to me by Dr. Shockley. A term in the energy involving y to the first power has consequently been omitted as its inclusion would have no bearing on the results here discussed.

In face-centered cubic alloys compounds of the form A_3B , AB , AB_3 may be described by a similar analysis.

F. BITTER

Massachusetts Institute of Technology,
Cambridge, Massachusetts,
April 18, 1938.

¹ W. Shockley, J. Chem. Phys. 6, 130 (1938).

Raman Effect in Liquid Acetylene

Faint rotation lines accompanying strong Raman frequencies have been reported in α -pinene¹ and in liquid acetylene.² Because only the P branches of the "rotation bands" were observed there has been continued conjecture as to the origin of these lines. In connection with this problem we have reinvestigated the Raman spectrum of liquid acetylene. And in exposures up to 16 hours with slit widths varying from 0.075 to 0.23 mm no rotation lines were found. These negative results along with the alternative explanation of the α -pinene band proposed in subsequent studies on α - and β -pinene³ militate greatly against the reality of such single-branched rotational effects.

One new line found by us corresponds to a shift of 1259 cm^{-1} . This is extremely diffuse in character and probably is an overtone of the deformation frequency at 630 cm^{-1} . Bhagavantam and Rao⁴ reported a shift of 1233 cm^{-1} excited by Hg 4358A which was not excited by Hg 4047A;

perhaps this is the corresponding shift in gaseous acetylene. Our shift was excited by both of the strong mercury lines.

Accompanying the strong 1961 cm^{-1} shift is a faint companion, 1934 cm^{-1} . These lines can be attributed to identical vibrations in the normal acetylene molecules and in the isotopic molecule $\text{HC}^{13}\equiv\text{C}^{12}\text{H}$. By application of the secular equation for acetylene given by Glockler and Wall⁵ with force constants adjusted to fit our data the position of this isotope lines was calculated to be 1929 cm^{-1} , which is only 5 wave numbers from the observed value. This same calculation indicates that the 3341 cm^{-1} frequency also should be accompanied by an isotope line, 3330 cm^{-1} . No line was observed here.

The 1961 cm^{-1} vibration as excited by Hg lines 4339, 4348, and 4358A ["the triplet"] along with the isotope line excited by 4358A show on the photographic plate in a somewhat regular order. And these lines all fit in the "rotation series" previously reported.² It must be noted, however, that two additional lines not found here were reported in that series.

In gaseous acetylene Bhagavantam and Rao measured a doublet 589 cm^{-1} and 643 cm^{-1} which they attributed to the O , P , R , and S branches (Q branch missing) of the Raman active degenerate deformation frequency. According to them, their interpretation checks with data on infra-red absorption in the gas. In the liquid, however, we do not obtain results strictly analogous. We have found lines at 560 cm^{-1} and 631 cm^{-1} ; the former is very weak as might be expected in view of the low temperature of observation (-75°C), but the greater doublet separation at this temperature would not be predicted. Moreover, another complication lies in the fact that the 631 cm^{-1} shift seems to consist of two distinct components when photographed under high dispersion. These are separated by 10–11 cm^{-1} with a mean value of 631 cm^{-1} . Such a splitting could not be predicted from the curves given by Bhagavantam and Rao on the construction of the doublet. These differences seem to be due to the different environment in the gaseous and liquid states.

The acetylene was prepared from pure calcium carbide, was purified by passing through a sodium plumbite-, chromic acid-, sodium hydroxide-, dehydrite-train; and by distillation.

The experimental data in summary lists the following Raman shifts: 560, 631 (625, 636), 1259, 1934, 1961, and 3341 cm^{-1} .

GEORGE GLOCKLER

MALCOLM M. RENFREW *

Institute of Technology,
University of Minnesota,
Minneapolis, Minnesota,
May 2, 1938.

¹ B. G. Bonino and P. Cella, Mem. Acad. Italia Chim. 2, 5 (1931).

² G. Glockler and C. E. Morrell, J. Chem. Phys. 4, 15 (1936).

³ S. K. K. Jatkari and R. Padmanabhan, Ind. J. Phys. 10, 55 (1936).

⁴ S. Bhagavantam and A. V. Rao, Proc. Ind. Acad. Sci. 3A, 135 (1936).

⁵ G. Glockler and F. T. Wall, J. Chem. Phys. 5, 813 (1937).

* M. M. Renfrew, DuPont Fellow, 1937–8.