

## Raman Effect in Liquid Ethylene and Ethane

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Citation: [The Journal of Chemical Physics](#) **6**, 409 (1938); doi: 10.1063/1.1750283

View online: <http://dx.doi.org/10.1063/1.1750283>

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pair of strong lines, 2235 and 2313  $\text{cm}^{-1}$  were explained by Badger<sup>4</sup> as manifestations of a single fundamental vibration interacting with an overtone of a lower fundamental in Fermi resonance due to accidental degeneracy. As a result, this carbon-carbon triple bond vibration frequency of the normal molecule appears split into two components, the actual fundamental frequency lying near the mean value of the pair. Similarly the weak pair of lines, 2201 and 2280  $\text{cm}^{-1}$ , are now considered to result from the interaction of the carbon-carbon triple bond fundamental of isotopic molecules with an overtone of a lower fundamental of these isotopic molecules.

By considering the normal molecule to be a simple harmonic two-body oscillator with reduced mass of  $1/\mu = 1/25 + 1/25$  and the isotopic molecule to have similar properties with a reduced mass of  $1/\mu = 1/25 + 1/26$  it is possible to calculate a separation of 20  $\text{cm}^{-1}$  for the carbon-carbon triple-bond frequencies of the normal and the isotopic molecules. This is not checked very well by the experimental measurement of 33  $\text{cm}^{-1}$  separating the mean values of the resonance split pairs. Of course this calculation is only an approximation. However, it must be emphasized that a close check is not to be expected since the separation of mean values of split frequencies does not give an accurate measure on separations of the "unsplit" carbon-carbon triple bond frequencies. The resonance split values observed depend not only on the "unsplit" fundamentals but also on the overtone of the lower fundamentals likewise engaged in the resonance interaction.<sup>5</sup> Because the isotopic shift for the lower frequency will differ from that for the higher frequency, the separation of mean values of split frequencies necessarily will vary from the separation of the true, "unsplit" fundamental vibrations in normal and isotopic molecules.

In the present approximate treatment no consideration was given to location of the  $\text{C}^{13}$ . In dimethylacetylene roughly four percent of the molecules are isotopic with half of these having isotopic triple bond carbons, the other half possessing  $\text{C}^{13}$  in the methyl groups.

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<sup>2</sup> G. B. Bonino and P. Cella, Nature 126, 915 (1930).

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<sup>5</sup> G. Placzek, *Handbuch der Radiologie*, Vol. 6 (Akad. Verlagsges. Leipzig, 1934), p. 326.

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### Raman Effect in Liquid Ethylene and Ethane

In the Raman spectrum of liquid ethylene two lines, 943 and 3075  $\text{cm}^{-1}$  have been observed<sup>1</sup> which have not been found in the gas on very long exposures at high pressure.<sup>2</sup> Since the work of Bonner<sup>3</sup> on Raman effect in the liquid and infra-red absorption in the gas, it has been customary in theoretical treatments<sup>4</sup> to use these lines (950 and 3069  $\text{cm}^{-1}$ ) as fundamental vibrations along with other frequencies including 940, 950, and 3107  $\text{cm}^{-1}$  which are infra-red active. According to the selection rules derived

for gases,<sup>5</sup> in molecules having a center of symmetry frequencies which are infra-red active should not appear in Raman effect. Of course there exists the possibility of an accidental coincidence of values. However, it is our belief that the appearance of the two lines mentioned in the Raman spectrum of liquid ethylene constitutes a violation of the selection rules since it seems likely that similar values in the infra-red absorption spectrum arise from the same vibrations.

The 3075  $\text{cm}^{-1}$  line is somewhat diffuse but is of such a strength that it certainly should be visible on reasonable exposures in the gas, if permitted there. The line cannot be interpreted readily as a combination or overtone. Hence it seems convenient to relate this line to the strong 3107  $\text{cm}^{-1}$  vibration observed in the infra-red. Of course, some increase in value is expected in going from liquid to gas for high frequencies. The increase here seems large, but does not appear excessive.

The 943  $\text{cm}^{-1}$  shift in Raman effect for the liquid is very diffuse, and it seems natural to identify this with the 940 and 950  $\text{cm}^{-1}$  lines in the infra-red. For low frequencies no great drop in value is observed generally in passing from gas to liquid.

Moreover, a similar comparison of data is possible with the Raman spectrum of liquid ethane and its infra-red absorption spectrum for the gas. In pure liquid ethane the Raman line 1463  $\text{cm}^{-1}$ , though diffuse, is well established.<sup>6</sup> However, in the gas Lewis and Houston<sup>7</sup> could not find it and although Bhagavantam<sup>8</sup> measured a shift in this neighborhood he was using an impure sample and considered the line observed to be due to a contaminant. Now in infra-red absorption experiments<sup>9</sup> strong bands are observed at 1465 and 1495  $\text{cm}^{-1}$ . Perhaps the mean value of 1480  $\text{cm}^{-1}$  for the gas corresponds to the 1463  $\text{cm}^{-1}$  Raman shift observed in the liquid.

In addition there are indications of a faint, diffuse Raman shift of 813  $\text{cm}^{-1}$  in liquid ethane which may be related to the infra-red band 827  $\text{cm}^{-1}$ .

Now it is possible that the failure to observe these Raman lines in the gas is due to their low intensities. But other lines of comparable strength (frequently of lower intensity) have been recorded in the gas. For this reason it seems likely that the Raman lines discussed are permitted only in the liquid state. The shifts are of nearly the same magnitude as infra-red active frequencies (see Table I), which fact may not be accidental. The presence of the  $\text{C}^{13}$  isotope has been shown to be responsible for slightly altered Raman shifts of low intensity accompanying corresponding strong lines excited in the normal molecules. The presence of this isotope contributes a small degree of asymmetry to the molecules which would cause infra-red active frequencies to be permitted in the Raman effect. However, such manifestations should be visible on long exposures in the gas as well as in the liquid. Since this condition has not been observed, it seems more reasonable to suppose that if the Raman and infra-red frequencies do belong to identical fundamentals, then a breakdown in selection rules in the liquid state for certain lines is indicated and must be due to the more strenuous environment existing there. Thompson and Linnett<sup>4</sup> have offered this

TABLE I.

SUBSTANCE	INFRA-RED (GAS)	RAMAN EFFECT	
		(LIQUID)	(GAS)
Ethylene	940	943	not found
	>945		
	950		
Ethane	3107	3075	not found
	827	813	not found
	1465	1463	? (8)
	>1480		
	1495		

suggestion in the case of ethylene, but for purposes of comparing calculated values with experimental data they considered the Raman lines in question to be bona fide Raman active fundamentals. Our experience adds weight to their tentative objections for the ethylene lines. Moreover, data given for ethane are substantiating. Perhaps theoretical treatments of the ethylene molecule will profit by including among the Raman active fundamentals one or both of the high frequency values, 3230 and 3263  $\text{cm}^{-1}$ , whose existence we have verified.<sup>1</sup>

Recently we have made more accurate evaluations on our plates for the Raman spectrum of liquid ethylene,

resulting in slight alteration of previously published values.<sup>1</sup> The new measurements are: 943 (1*d*), 1341 (10), 1602 (0.5), 1621 (7), 1653 (1), 2870 (2), 2997 (0.5), 3008 (10), 3075 (2*d*), 3230 (0.5), 3263 (0.5). The estimated intensities are in parentheses.

The 1602  $\text{cm}^{-1}$  shift is the carbon-carbon vibration in the isotopic molecule  $\text{H}_2\text{C}^{13}=\text{C}^{12}\text{H}_2$ . The shift 2997  $\text{cm}^{-1}$  probably also is due to this isotopic molecule, the separation from the 3008  $\text{cm}^{-1}$  vibration of the normal molecule being checked roughly by calculation. However, the accuracy of measurement has been diminished by the lack of clear resolution of the weak and strong line. Our value for the isotope line probably is low.

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<sup>1</sup> G. Glockler and M. M. Renfrew, J. Chem. Phys. 6, 170 (1938).

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