

Vibrational Spectroscopy of CS₂

A Physical Chemistry Experiment

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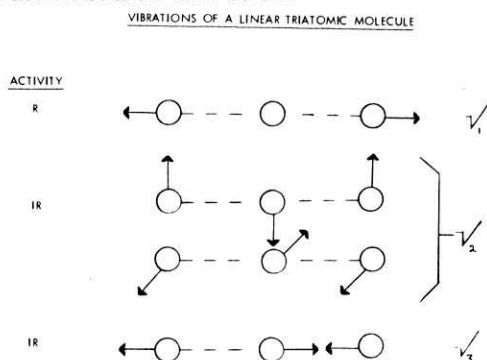
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We have found a need for an experiment in vibrational spectroscopy which goes beyond the usual infrared rotation-vibration spectrum of HCl as described in Shoemaker, Garland, and Steinfeld (1). However, it is difficult to find spectra of polyatomic molecules which may be analyzed at a reasonably unsophisticated level (e.g., without a normal coordinate calculation). The spectra should be of sufficient complexity so that many of the features observed in larger molecules may be meaningfully illustrated. The obvious choice, CO₂, does not lend itself to simple analysis because of the strong Fermi resonance which causes the overtone of the bending vibration to couple with the symmetric stretching mode (2), thereby giving rise to a spectral feature not easily explained at an elementary level. In addition, gas phase spectra require cells of a somewhat specialized nature. We have found that CS₂ in the liquid state is a reasonable choice for illustration of the following phenomena:

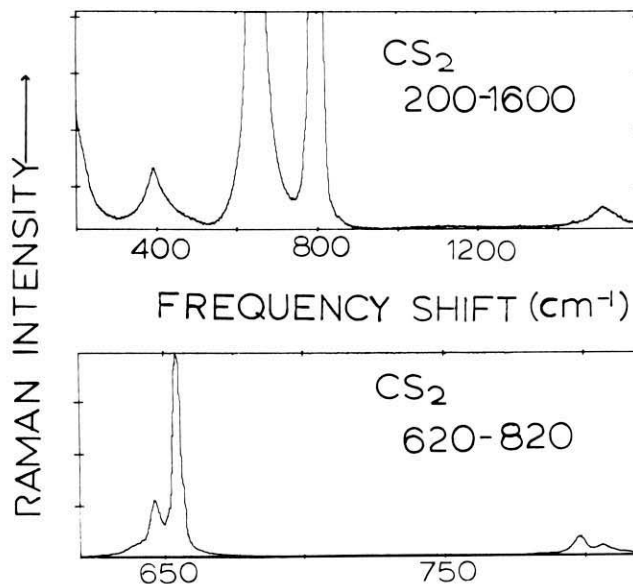
- 1) Rule of Mutual Exclusion between IR and Raman spectra for centrosymmetric molecules.
- 2) Violation of same in the liquid state.
- 3) Observation of certain types of vibrational bands not found in diatomic molecular spectra such as combination and difference bands.
- 4) Simple calculations in going from the set of fundamental frequencies to molecular parameters (bending and stretching force constants) of some interest with regard to chemical bonding. The experiment may either be carried out as a "dry lab", or the students may be permitted to obtain IR and/or Raman spectroscopic data.

Theory

The four fundamental vibrations of linear centrosymmetric molecules are classified according to the $D_{\infty h}$ point group. The nature of the expected vibrations as well as their IR and Raman activities are shown below:



We have found that class discussions of IR and Raman activity are greatly facilitated by reference to ν_1 and ν_3 , the symmetric and antisymmetric stretching modes, respectively. The absence of a change in the dipole moment and hence the inactivity of ν_1 in the IR spectrum can be demonstrated easily without recourse to the character table. The strong Raman activity of ν_1 as demonstrated by a change in the molecular polarizability during this motion, can be rationalized if the concept of polarizability is related to the ease of deforming the electron cloud from its equilibrium shape around the nuclei. Similar considerations (with opposite conclusions regarding activity) can be gleaned from ν_3 .



Raman spectroscopic data for CS₂ liquid form. *Top*: 200–1600 cm⁻¹ spectral region. *Bottom*: An expanded spectrum of the 620–820 cm⁻¹ region. Excitation, 100 mw of 5145 Å; resolution, *top*—about 2 cm⁻¹, *bottom*—about 1 cm⁻¹; sample was examined in a capillary mounted in the transverse mode.

Several features in addition to the expected fundamentals are observed in both the IR and Raman spectra. While the rule of mutual exclusion is expected to hold rigorously for molecules in the gas phase, collisions between molecules in the liquid state produce instantaneous deviations from the $D_{\infty h}$ point group; hence, the rule of mutual exclusion becomes approximate. For example, ν_2 and ν_3 , expected to be Raman inactive, actually appear as weak features with intensities less than 5% of that of ν_1 . Similarly, ν_1 appears in the IR spectrum as an extremely weak feature. Also present in the IR and Raman spectrum are a variety of overtone, combination, difference, and hot bands, whose assignment forms part of the exercise associated with this experiment.

Experiment

The IR data can be obtained on any available spectrophotometer. A variety of path lengths from 0.1 to 10mm are needed to observe, with reasonable intensity, the large number of spectral features. It is advantageous to have an instrument with a range extending to below 400 cm⁻¹, in order that the bending vibration at 391 cm⁻¹ can be observed. KBr is a relatively inexpensive window material which, although beginning to absorb near 391 cm⁻¹, still allows observation of that frequency. In order to observe on scale the very intense ν_3 motion, either a very thin cell or suitable solvent must be used. If this is inconvenient, the frequency may be obtained from the Raman data.

CS₂ is a very strong Raman scatterer and the spectrum may easily be obtained on any commercial instrument. If Raman equipment is not available, copies of the 200–1600 cm⁻¹ region as shown in the figure, may be used. We would be pleased to send enlarged versions on request.

Spectroscopic grade CS₂ was used in the experiment. Note that CS₂ is both **very toxic** and **malodorous**, and students should be given clear instructions for its safe handling. The observed spectral data

and assignments (4) are collected in the table. The IR spectrum was calibrated with polystyrene; the Raman spectrum was calibrated with emission lines from a neon lamp. Accuracy is $\pm 2 \text{ cm}^{-1}$ in either case.

Data Treatment

The students were asked to treat the data in the following manner: From ν_1 , ν_2 , and ν_3 they were expected to suggest possible assignments of the other observed features as combination bands, overtones, etc. Furthermore, using the equations in Herzberg (3) for a valence force field, they were asked to calculate two independent values for the C=S stretching force constant k_1 and for the bending force constant k_5/L^2 .

Depending on the time available and the sophistication of the students, some or all of the following additional experiments and calculations may be feasible. The mid-IR gas phase spectrum of CS_2 may be obtained. Although the rotational structure cannot easily be resolved, the absence of a Q branch for ν_3 , and its presence for ν_2 , indicate these modes to be parallel and perpendicular vibrations respectively. This observation provides further evidence for the linearity of the molecule.

Although the rotational transitions may not be resolved easily, formulas for the intensity distribution in the P and R branches (5) give for the separation of the maxima

$$\Delta\nu_{P-R} = 2.358\sqrt{T \cdot B} \quad \text{In units of cm}^{-1}$$

An estimate for B and therefore for the bond length of the molecule may be obtained.

Finally, calculated values for the stretching force constant k_1 vary slightly depending upon whether the equation for ν_1 or ν_3 is used. Students interested in pursuing the source of this difficulty may be introduced to interaction constants such as those described in Wilson, Decius and Cross (6).

Literature Cited

- (1) Shoemaker, D. P., Garland, C. W., and Steinfeld, J. I. "Experiments in Physical Chemistry" 3rd ed., McGraw-Hill, Inc., New York, 1974, p. 450.
- (2) Herzberg, G., "Infrared and Raman Spectra" D. Van Nostrand, Co., Princeton, N.J., 1956, p. 272.
- (3) Reference (2), p. 172.
- (4) Ribnikar, S. V., and Puziç, O. S., *Spectrochimica Acta*, **29A**, 307 (1973).
- (5) Reference (2), p. 391.
- (6) Wilson, E. B., Jr., Decius, J. C., and Cross, P. C. "Molecular Vibrations" McGraw Hill, New York, 1955, p. 177.
- (7) Evans, J. C., and Bernstein, H. J., *Can. J. Chem.* **34**, 1127 (1956).

Infrared and Raman Frequencies in Liquid CS_2 —300–3000 cm^{-1} region

Observed ^a	This work ^b	Lower State			Upper State			Intensity ^c
		ν_1	ν_2	ν_3	ν_1	ν_2	ν_3	
390.5	390 (IR)	0	0 ⁰	0	0	1 ¹	0	S
	393 (R)							W
652.5	647 (R)	0	1 ⁰	0	1	1 ⁰	0	M
	654 (IR)	0	0 ⁰	0	1	0 ⁰	0	W
	655 (R)							VVS
710		0	2 ⁰	0	0	0 ⁰	1	
788	798 (R)	0	0 ⁰	0	0	2 ⁰	0	VS
807	806 (R)	0	1 ⁰	0	0	3 ¹	0	M
	814 (R)							W,Sh
855.1	855 (IR)	1	0 ⁰	0	0	0 ⁰	1	W
915		0	1 ¹	0	2	0 ⁰	0	
1039		0	0 ⁰	0	1	1 ¹	0	
1197.4		0	0 ⁰	0	0	3 ⁰	0	
1306		0	0 ⁰	0	2	0 ⁰	0	
1508	1513 (R) ^d	0	0 ⁰	0	0	0 ⁰	1	VW
	1522 (IR)							VVS
1903		0	0 ⁰	0	0	1 ¹	1	
2151.7	2152 (IR)	0	0 ⁰	0	1	0 ⁰	1	S
2291.4	2294 (IR)	0	0 ⁰	0	0	2 ⁰	1	
2799.6	2799 (IR)	0	0 ⁰	0	2	0 ⁰	1	VW
2922.8		0	0 ⁰	0	1	2 ⁰	1	

^a Observed features and assignments of upper and lower states are taken from reference 4.

^b The IR bands listed are those observed by us in a 0.1 mm KBr cell. Some features which are listed in reference (4) as arising from ^{13}C or ^{34}S isotopes, or require solution spectra (narrower bands) in order to be completely resolved, have been omitted from the Table.

^c W = weak, M = medium, S = strong, Sh = shoulder, V = very.

^d IR frequency is from a CCl_4 solution of CS_2 . Most of the observed vibrational bands have greatly reduced halfwidths in CCl_4 solution compared with pure liquid. In addition, frequencies in solution are much closer to their gas phase values than are pure liquid frequencies. This has been attributed to lowering of symmetry in the pure liquid phase (7).