

Internal Rotation V. The Energy Difference between the Rotational Isomers of 1,2 Dibromoethane

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Clusius⁸ showing the effect of pressure on the heat capacity of the liquid near the λ -point, it is seen that the λ -point shift of the adsorbed helium is in such a direction as to indicate large pressure effects for the first layers, this pressure decreasing with increasing adsorption. What is more, the λ -point for 5-6 layers occurs at about 1.85°K which corresponds to a pressure of about 25 atmos. for bulk helium. This is approximately the point at which the λ -line intersects the solid curve in a P, T diagram. Corresponding to this, there is no λ -point for the 3-4 layer coverage according to Frederikse's data, indicating that the film has become "solid." Further observation shows that the heat capacities of the adsorbed films are higher than the liquid below the λ -point and lower than the liquid above the λ -point. This is the case as well for bulk helium under pressure with the direction and magnitude of the effect in agreement with the λ -point shift pointed out above. These shifts in the λ -point can be used for calculating the pressure in the upper layers from the peak in the heat capacity curves. This will be useful information in developing any statistical model of the helium film and for using this model in the calculation of heats of adsorption, etc. It may be well to point out that a first-order transition corresponding to fusion in bulk helium would be expected somewhat above 4°K at low coverages where the pressure corresponds to several hundred atmospheres.

¹ Long and Meyer, Phys. Rev. **68**, 440 (1949).

² Schaeffer, Smith, and Wendell, J. Am. Chem. Soc. **71**, 863 (1949).

³ Brunauer, Emmett, and Teller, J. Am. Chem. Soc. **60**, 309 (1938).

⁴ W. Band, Phys. Rev. **68**, 441 (1949).

⁵ T. Hill, J. Chem. Phys. **14**, 263 (1946); **14**, 268 (1946); **15**, 757 (1949).

⁶ H. P. R. Frederikse, Physica **XV**, No. 10, 860 (1949).

⁷ The number of layers in Frederikse's paper is calculated on the basis of He-He spacing in the liquid rather than v_m calculated from the B.E.T. equation. If the v_m calculated from the B.E.T. equation be used what is here called 4 layers is actually about one layer. It is difficult to correct the other layers for this effect. However, no quantitative conclusions can be reached in any case since the contribution to the heat capacity of each layer should be graphed against temperature to detect the λ -point in each layer whereas Frederikse graphs the total heat capacity against temperature. Such a procedure would give larger areas under the curves for the λ -point-region but does not change the position of the peaks much as shown by a rough treatment of Frederikse's data.

⁸ W. H. Keesom and K. Clusius, Proc. Roy. Soc. Amst. **34**, 605 (1931).

Internal Rotation V. The Energy Difference between the Rotational Isomers of 1,2-Dibromoethane

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April 17, 1950

THE isomerization energy for the rotational isomers of 1,2-dibromoethane has been obtained by the spectroscopic method by Mizushima *et al.*¹ and found to be 1450 cal./mole.

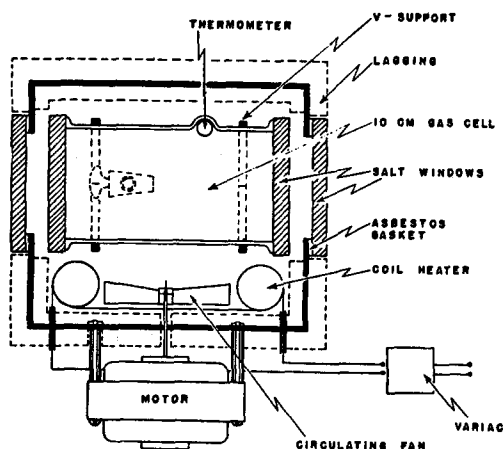


FIG. 1. Apparatus.

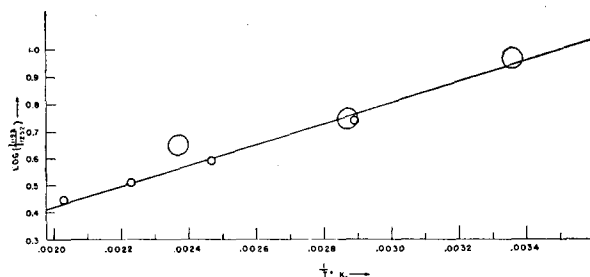


FIG. 2. Plot of log ratio of intensities against $1/T$. The large circles are for a pressure of 10 mm of Hg in a 10-cm cell. The small circles are for a pressure ≈ 60 mm of Hg in a 10-cm cell.

They obtained this energy (1400 cal./mole) also by measurement of the electric moment as a function of temperature. Gwinn and Pitzer,² also, have investigated this molecule by measurement of the electric moment as a function of temperature and find a value of 1.5 cal./mole for the energy difference.

With a specially constructed cell, the plan of which is shown in Fig. 1, the infra-red spectra of gaseous $C_2H_4Br_2$ have been obtained from 25° to 250°C. The thermometer extends into the gas cell through a ground glass joint so that its bulb is in about the middle of the cell, but well out of the path of the beam from the Globar. The cell as shown in Fig. 1 is covered with a close fitting lid when in use. A Perkin-Elmer (Model 12C) infra-red spectrometer was used in conjunction with a Brown recorder to obtain the spectra.

The ratio of the intensity (area under the density curve) of the band at 1192 cm^{-1} to that of the band at 1252 cm^{-1} gives the ratio of the number of *trans*-molecules (C_{2h}) to the number of *gauche* molecules (C_2).³ The plot of $\ln \frac{\text{intensity of } 1252\text{ cm}^{-1}}{\text{intensity of } 1192\text{ cm}^{-1}}$ against $1/T$ gives $\Delta H/R$ for the temperature range investigated.³ Figure 2 shows this straight line plot, the slope of which gives $\Delta H = 1770 \pm 150$ cal./mole.

Other molecules with rotational isomers being investigated here by the spectroscopic method include $CH_2Cl-CHCl_2$, $CHCl_2-CHCl_2$ and isopentane.

¹ Mizushima, Morino, Watanabe, Simanote, and Yamagouchi, J. Chem. Phys. **17**, 591 (1949).

² W. D. Gwinn and K. S. Pitzer, J. Chem. Phys. **16**, 303 (1948).

³ H. J. Bernstein, J. Chem. Phys. **17**, 258 (1949).

On Discrimination in Mass Spectrometer Ion Sources

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April 19, 1950

DISCRIMINATION in mass spectrometer ion sources has been studied by Coggeshall,¹ and the following theoretical curve for peak heights vs. ion accelerating voltage has been given:

$$I = pA \left\{ 4.46 - \frac{1}{2} \frac{1}{(V_1 + V_2)^{1/2}} \frac{z}{d} \right\},$$

where I is the ion current intensity, p the true abundance in the gas sample, z the distance among the slits in the source, d the half-width of the second slit and A a constant. The accelerating voltages V_1 and V_2 are respectively the voltage carrying the ions out of the electron path, and the proper accelerating voltage of ions; in practice V_1 is some hundredth part of V_2 .

A 60° Nier-type² mass spectrometer for light elements which we have built in this laboratory for routine work has been arranged in order to test experimentally Coggeshall's theory, and to find out whether other parameters also occur which influence

the ion current intensities at different accelerating voltages. Our results, which are reported more extensively elsewhere,³ point to a stronger discrimination than indicated by the theory, and, furthermore, to a sharp dependence on V_1 , the first low accelerating voltage in spite of Coggeshall's assumption. Discrimination curves, obtained at several V_1 constant values, show that a lower discrimination is had with the same V_1 values for which the ion current is stronger.

Wide variations of electrons accelerating voltage and trap voltage (between 22.5 and 135 volts, and 22.5 and 90 volts respectively) do not influence discrimination. Gas pressure variation in the ion source can also produce a different discrimination, but a quantitative measurement of this effect is contrasted by the difficulty of reproducing the same pressure conditions; we can say that discrimination becomes larger at increasing pressure. Gases used were N_2 and H_2 ; a doubtful mass influence is discussed in reference 3.

As a conclusion we can say that the theory is lacking, and that an experimental discrimination curve may be used only if gas pressure conditions are as far as possible reproduced in the ion source. As we have also tested, the way to obtain true and well-reproducible measurements is to operate by magnetic scanning.

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¹ N. D. Coggeshall, *J. Chem. Phys.* 12, 19 (1944).

² A. O. Nier, *Rev. Sci. Instr.* 18, 398 (1947). During these measurements the ion source was reduced to Coggeshall's simplified model.

³ G. Careri and G. Nencini, *Nuovo Cimento* 7, 64 (1950).

On the Elimination of Extraneous Scattering in Raman Spectra

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April 3, 1950

IN view of the increased theoretical and practical importance of fluorocarbons, it is desirable to obtain their Raman spectra as completely as possible. It was in regard to low boiling fluorocarbons that the procedure referred to in this letter was developed.¹ As a class, these compounds are especially troublesome in that nearly all of them exhibit weak Raman scattering. One can expect their Raman spectra to be only about $\frac{1}{10}$ the intensity of those of the corresponding hydrocarbons.

The conventional approach to the problem of background reduction has been through the use of light filters; in work with fluorocarbons, however, dependence on filters alone leaves much to be desired. Runs made in this research were in the liquid phase without filters except those used for special effects such as polarization or suppression of the lower exciting lines. Results obtained point to the possibility that nearly all of the background commonly observed with lengthy exposures is due to light sent into the spectrograph through simple reflection of normal arc continuum by physical contaminants in the Raman sample; Rayleigh scattering of arc continuum is rarely the limiting factor. These contaminants include dust, small particles of drying agent and especially particles of near colloid size of undetermined composition which are commonly present in many chemically pure compounds. The degree of physical purity here achieved has been such that (1) liquefied samples could be greatly superheated before boiling occurred, (2) microscopic examination showed no particles present, and (3) observation of the liquid along the long axis of the Raman tube showed no trace of haze, the liquid appeared optically void under the most severe lighting conditions obtainable. One of the compounds investigated was octafluoropropane.² It is believed that 22 of its 27 theoretical fundamentals were observed; Herzberg³ lists only 13 lines for propane.

In the region between Hg 4358A and the position normally occupied by the highest CH vibration, 27 distinct Raman lines were observed for octafluoropropane, 5 of which probably arose

from Hg 4339 and 4348A. In this same region 36 lines were seen for methylfluoroform, 21 of which seemed due to exciting lines lower than Hg 4358A, still others arose from combinations or overtones. With properly prepared samples these lines could be clearly seen virtually free from background.

The Raman tubes were cleaned in the usual way but were then flushed with a non-soap detergent solution and steam. This was done in such a manner that once steam stopped flowing, steam condensing inside the system did not draw in dust laden air. Water was removed from the system as vapor by vacuum pumps and the system thereafter kept under vacuum.

The samples were dried in the gas phase by barium oxide drying agent.⁴ Phosphorus pentoxide could not be used since samples were invariably contaminated by contact with it and gave high background spectrograms.

The Raman samples were freed of colloidal impurities by slow vacuum evaporation through fritted glass barriers at a temperature 40 degrees or more below their atmospheric boiling points. This step and that of steam flushing were both tedious and time consuming, however, it was possible by such procedure to secure background free spectrograms without the use of filters even though exposure times were used which caused photographic halos to form around the stronger Raman lines. With optically void samples, background reducing filters can be used to greater advantage than commonly supposed and permit exposures of extreme length.

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¹ Based on a portion of a thesis presented by H. Dean Mallory in partial fulfillment of the requirement for the degree of Doctor of Philosophy in the Graduate School of the State University of Iowa (February, 1950).

² Edgell, Mallory, and Weiblen, "The raman and infra-red spectra of octafluoropropane" (to be published).

³ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, (D. Van Nostrand Company, Inc., New York, 1945).

⁴ Barium and Chemicals, Inc., Willoughby, Ohio.

The Infra-Red Spectra of Hydrogen and Deuterium Peroxides in Condensed Phases*

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April 24, 1950

THE investigations of the vibrational spectrum of hydrogen peroxide, particularly in the region of fundamentals, have not been numerous and a high percentage of the reliable data are for the liquid phase. On the basis of the available information, there seem to be two main points of interest. First, the frequency corresponding to the torsional motion of the OH groups around the O—O axis has not been conclusively identified, and secondly, no completely satisfactory assignment has yet been proposed for an infra-red band observed in the neighborhood of 2800 cm^{-1} . The assignment of frequencies is somewhat complicated by the fact that extensive hydrogen bonding occurs in the liquid causing greatly broadened lines and marked temperature shifting of bands involved in hydrogen motions.

Recently, Giguère¹ has reported the results of an investigation of the infra-red spectrum of the vapor of hydrogen peroxide and also of the liquid at room temperatures. In the liquid, a rather broad region of absorption with a maximum at about 550 cm^{-1} was noted.[†] This band was tentatively assigned to the torsional mode and the band observed at 2780 cm^{-1} in the liquid was then suggested to be a triple combination frequency involving ν_3 , the O—O stretching mode, ν_2 , the symmetrical bending mode, and the newly found torsional mode at 550 cm^{-1} .

The present work was begun following an investigation of the Raman spectrum of hydrogen and deuterium peroxides.² Inasmuch as it has now been interrupted, it appears desirable to report the data obtained in a preliminary fashion in view of the general interest in this compound.