

## Raman Spectrum of Thiophosgene

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temperature, as certain sets of vibrational frequencies will make  $T$  negative or experimentally out of reach.

The parallelism between the absorbability of the hydrogen isotopes and the rate with which they hydrogenate ethylene has been pointed out by Beebe and Klar.<sup>1, 2</sup> On nickel the ratio  $\alpha$  of

the rate of the light hydrogen reaction to the heavy hydrogen reaction actually "turns over" in the region of the inversion temperature, while on copper<sup>4</sup> between 0°C and 300°C  $\alpha$  falls from 2.07 to approximately unity.

<sup>4</sup> Wheeler and Pease, J. Am. Chem. Soc. **58**, 1665 (1936); **57**, 1144 (1935).

## LETTERS TO THE EDITOR

*This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must*

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### Raman Spectrum of Thiophosgene

In an analysis of the ultraviolet absorption spectrum of thiophosgene it became desirable to know the vibration frequencies of the molecule. Each of the six normal vibrations should be excited in the Raman spectrum, which was accordingly measured, using the liquid substance. The exciting frequency was the 5876Å line of a specially constructed helium discharge lamp, though a few lines scattered from the 6678Å helium line gave corroborative data. The spectrograph was a large aperture glass prism instrument giving a dispersion of about 100Å/mm in the region involved. The H $\alpha$  and neon lines were used as standards. The following frequencies, (cm<sup>-1</sup>) with rough relative intensities, were found: 200 (1), 287 (3), 363 (1), 496 (5), 660 (0), 1121 (10), 1388 (2). Using the same nomenclature as has been given for the case of phosgene,\* the three relatively intense symmetric vibrations are assigned as follows:  $\nu_1=1121$ ,  $\nu_2=496$ ,  $\nu_3=287$ . The two antisymmetric planar vibrations will probably be  $\nu_4=660$ ,  $\nu_5=363$ , and the nonplanar oscillation  $\nu_6=200$ . It seems probable that the Raman interval 1388 is to be interpreted as due to the excitation of the combination ( $\nu_1+\nu_3$ ). A preliminary survey of the infra-red spectrum of thiophosgene vapor confirms the above values both as regards magnitude and assignment. The analysis of the ultraviolet absorption band system reveals that the most prominently excited vibrations are the symmetrical ones. The details of the ultraviolet and infra-red data will shortly be published, as well as a comparison with the corresponding data for formaldehyde and phosgene, and a discussion of the force constants in these molecules.

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\* Bailey and Hale, Phil. Mag. **25**, 98 (1938).

### Statistical Mechanics of Mobile Monolayers

Following a suggestion to the writer by Professor R. H. Fowler, the methods of Mayer and Ackermann<sup>1, 2</sup> giving

the saturated vapor pressure curves for condensing systems have been adapted to the problem of mobile monolayers. The problem is simplified as an example in the theory of dissociating (clustering) assemblies,<sup>3</sup> and the equation giving the saturated vapor tension  $F_c$  and the critical area  $A_c$  for a monolayer of  $X$  molecules is easily found to be of the form

$$F_c A_c / X k T = (1 + \nu) / (1 + \sigma),$$

where  $\nu$  and  $\sigma$  are sums which can be evaluated in terms of the molecular fields. For the latter, point functions of the radius alone are useless, but it is found sufficient to specify only the number of bonds with nearest neighbors and the mean energy per bond. Good agreement is obtained with the data of Adam and Jessop on the fatty acids<sup>4</sup> by assuming six bonds with mean energy  $3.8 \times 10^{-14}$  erg per bond, for the vapor-duplex change at large molecular areas. And in myristic acid for the duplex-liquid change at small molecular areas good agreement is found with the modified duplex equation

$$(F_c - F_0)(A_c - A_0) / X k T = (1 + \nu) / (1 + \sigma)$$

with six bonds of mean energy  $5.6 \times 10^{-14}$  erg per bond, provided the spreading effect of the liquid surface is

$$F_0 = -11.2 \text{ dynes/cm}$$

and the area occupied by the clustered molecules is

$$A_0 = (14 + 0.2t)X,$$

where  $t$  is the temperature in degrees Centigrade. This last agreement is supporting evidence for Langmuir's duplex theory of the expanded film.<sup>6</sup>

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August 8, 1938.

<sup>1</sup> Joseph E. Mayer, J. Chem. Phys. **5**, 67 (1937).

<sup>2</sup> Mayer and Ackermann, J. Chem. Phys. **5**, 74 (1937).

<sup>3</sup> W. Band, J. Chem. Phys. **6**, 654 (1938).

<sup>4</sup> Adam and Jessop, Proc. Roy. Soc. **A110**, 423 (1926).

<sup>5</sup> Adam and Jessop, Proc. Roy. Soc. **A112**, 362 (1926).

<sup>6</sup> Langmuir, J. Chem. Phys. **1**, 769 (1933).