*S*1·18. **The influence of thermal motion on structure determination of linear molecules using the electron-diffraction method.** By O. BASTIANSEN & M. TRÆTTEBERG, *Institutt for teoretisk kjemi, Norges tekniske Høgskole, Trondheim, Norway.*

In the study of dimethyldiacetylene it was discovered that the observed non-bonded C–C distances were shorter than that calculated summing up the observed bond distances. Though the effect was small it appeared to be real, and it was attributed to out-of-linearity vibrations. It was found worth while to study this effect in other molecules with linear equilibrium conformation. The effect has been observed in allene and butatriene, and for these molecules quantitative data for the effect were obtained. If the effect is neglected, linear molecules appear bent. The out-of-linearity vibrations will complicate structure determinations of linear molecules using a spectroscopic method based upon measurements of moments of inertia. The average moment of inertia about an axis perpendicular to the molecule will be a trifle smaller than for the presumed stiff model.

The effect might obscure electron-diffraction determination of slightly bent molecules, as these are difficult to distinguish from linear molecules with a large out-of-linearity amplitude of vibration. One case that was supposed to be on the limits of the two alternatives is presented by the molecule of disilylether studied by V. Ewing. It can be shown that this molecule is most likely bent also in the equilibrium conformation.

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*S*1·19. **Structure anomalies and molecular vibrations in carbon suboxide.** By H. BREED, O. BASTIANSEN & A. ALMENNINGEN, *Institutt for teoretisk kjemi, Norges tekniske Høgskole, Trondheim, Norway.*

The sector method of electron diffraction has been used to reinvestigate the molecular structure of carbon suboxide throughout the range of s from 2 to 65 Å^{-1} (where $s=(4\pi/\lambda)\sin\theta$). Fourier transformation of this data shows the C=C distance well resolved from the C=O distance. The overall length of the molecule, and the distances from first to third, and first to fourth atoms are distinctly less than the sum of the individual component C=O and C=C distances. The effect is reproduceable and more than an order of magnitude larger than the uncertainties in the experiment. In carbon suboxide the effect is larger than that observed in allene, butatriene, and dimethyldiacetylene. Carbon suboxide seems to represent a case where it is difficult to distinguish between a linear molecule with a large out-of-linearity amplitude of vibration, and a molecule with bent equilibrium configuration.

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*S*1·20. **The effect of temperature on the mean square amplitudes of vibration of PCl_3.** By KENNETH HEDBERG & MACHIO IWASAKI, *Department of Chemistry, Oregon State College, Corvallis, Oregon, U.S.A.*

Although one expects an increased temperature to increase the mean square amplitudes of vibration of molecules, the effect is too small to have been evident from electron diffraction data in the past. Recent improvements in experimental techniques, however, yield accurate intensity data over a much larger scattering angle, and it seemed worthwhile to investigate the effect of temperature anew.

Our data were taken at 27 and 232 °C. in the Norwegian apparatus from gaseous PCl_3, a molecule of well-known structure and thoroughly studied vibrational spectrum, and with atoms of atomic numbers so close as to make the effect of phase shift negligible. The data were reduced in the usual way and radial distribution curves calculated from the resulting intensity curves.

We find PCl_3 to have the same structure, within experimental error, at the two temperatures ($r_{P-Cl}=2{\cdot}039$ and 2·044 Å, and $r_{Cl\cdots Cl}=3{\cdot}131$ and 3·138 Å at 27 and 232 °C., respectively (in good agreement with the corresponding ground state microwave values 2·043 and 3·134 Å); however, there is a considerable difference in the root mean square amplitudes of vibration for both the P–Cl and Cl · · · Cl distances: at 27 °C. the preliminary values are respectively 0·050 and 0·081 Å, and at 232 °C. 0·059 and 0·111 Å. These results are in fairly good agreement with prediction from spectroscopic data.

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*S*1·21. **Determination of potential constants for PCl_3 from gaseous electron diffraction data and normal vibration frequencies.** By MACHIO IWASAKI & KENNETH HEDBERG, *Department of Chemistry, Oregon State College, Corvallis, Oregon, U.S.A.*

Vibrational potential constants are usually determined from the frequencies of normal vibrations. Most often these are not sufficient to determine constants for a general quadratic potential function, so that either a simplified field must be assumed or data must be obtained for isotropic species.

The recent developments in gas phase electron diffraction techniques have made it possible to determine mean square amplitudes of vibration with high accuracy and it has been shown that these are in generally good agreement with those calculated from assumed potential functions. But it seems especially attractive to combine the mean amplitudes of vibration from electron diffraction with the vibrational frequencies and to attempt to determine potential constants directly.

PCl_3 was chosen for this study because (1) the complicating phase shift is negligible (see preceeding abstract), (2) the geometry is quite favorable, i.e., the chlorine atoms are far enough apart so that steric effects, which might be reflected in distorted radial distribution curve peak shapes, would be small and (3) the four well-known vibrational frequencies and the two mean square amplitudes permit evaluation of the six constants in the general quadratic potential function. The procedure was to calculate the values of the root mean square displacements for each distance with the four fundamental frequencies by methods similar to those described by Morino, Kuchitsu & Shimanouchi (*J. Chem. Phys.* (1952), **20**, 726) or Cyvin (private communication). Contours corresponding to these values were plotted as a function of two convenient potential constant parameters for comparison with the observed values. We find that our preliminary observed values of 0·050 and 0·081 Å for