

14.X-07 DYNAMIC EFFECTS IN GAS ELECTRON DIFFRACTION: EXPERIMENT AND THEORY. By L. S. Bartell, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, U.S.A.

If waves are scattered sufficiently weakly by individual atoms, the total scattering from an array of atoms may be accurately described by kinematic theory. This theory, which neglects any phase shift or attenuation by scattering of a primary wave as it propagates through an array, and neglects multiple scattering, may hold adequately for X rays diffracted by arrays as large as macroscopic crystals. On the other hand, it can fail conspicuously for electrons scattered by an array as small as a single molecule. Because gas-phase electron diffraction interpretive routines are generally based on the "semikinematic" theory advanced by Schomaker and Glauber (Nature (1952) 170, 291), which includes only intra-atomic multiple scattering while neglecting inter-atomic, it is worthwhile to review principles and consequences of dynamic scattering. The theoretical approach most convenient for treating the scattering of 40 keV electrons by randomly oriented molecules differs from those suitable for slow electrons (where the problem is even more acute) and for X-ray crystallography. A reasonably satisfactory solution simple enough for routine use in analyses has been developed (Miller and Bartell, J. Chem. Phys. (1980) 72, 800). Although the need for corrections was first apparent in the case of molecules with heavy atoms (e.g. UF₆ and ReF₆), it turns out that effects are by no means negligible for molecules as light as SF₆ and CCl₄. What influence the neglect of dynamic corrections can be expected to have on derived structures and amplitudes of vibration will be discussed.

14.X-08 STRUCTURE OF INORGANIC FREE MOLECULES.

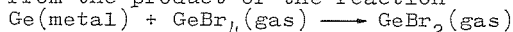
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There is an abundance of structural variety of inorganic compounds in the vapour phase. High-temperature vapours are especially rich in various interesting species. Electron diffraction is practically the only tool to elucidate their molecular geometry.

The main experimental difficulty is to achieve the desired and well-defined vapour composition. The combined high-temperature electron diffraction - quadrupole mass spectrometric experiment opens new possibilities in this area.

Currently a set of diffraction data is being analysed from the vapour of manganese bromide which contained an appreciable amount of dimeric species Mn₂Br₄ in addition to the prevailing monomeric species MnBr₂.

The combined experiment also facilitates the investigation of unstable species. Thus, e.g., a structure analysis of germanium dibromide is under way on the electron scattering data from the product of the reaction



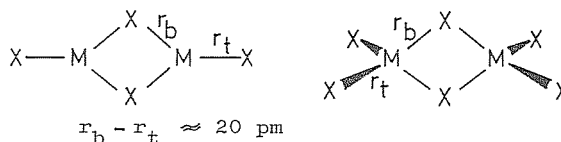
An interpretational difficulty originates from the large-amplitude intramolecular motion. Linear chains and planar rings appear as bent and puckered average configurations. It is necessary to supplement the electron diffraction data with spectroscopic information. Conversely, the electron diffraction results may facilitate the understanding and extension of spectral information.

Some findings of interest:

-The first row transition metal dihalides show bond length variations that correlate with the electron density distribution of these molecules. Considerations of the environmental symmetries as regards the M atom in the gas-phase MX₂ dihalides, have been used

recently [M. Hargittai, Inorg.Chim.Acta Lett. in press] to predict the trend of their bond length variation. The largest deviation of the M-X bond lengths from that expected for atoms M with spherically symmetrical d electron distribution have been predicted for Cr and Cu. A preliminary result of $r(\text{Cr-Cl}) = 217 \text{ pm}$ in CrCl₂ is consistent with this notion [I. Hargittai, Gy. Schultz, J. Tremmel, unpublished].

-The dimeric species of transition metal dihalides, M₂X₄ have a four-member bridge structure in which the terminal and bridge bond lengths are related similarly as those M₂X₆ dimeric metal halide molecules.



-Electron pair repulsions seem to be important in the structural variations of the GeX₂ (X = F, Cl, Br) series. The available experimental data on AF₂ (A = C, Si, Ge) and GeX₂ make it possible to predict the geometries for other carbene-analogs: CCl₂, CBr₂, SiCl₂, SiBr₂.

14.X-09 INTRAMOLECULAR DEFORMATIONS IN ORGANIC MOLECULES. By F.C. Mijlhoff, Gorlaeus Laboratories, State University, Leiden, The Netherlands.

Superposition of a number of conformations is widely used as a method of constructing models for the interpretation of structural data for gas phase molecules performing large amplitude motions. Usually the structural parameters are assumed to be independent of the soft internal coordinate. Quantum chemical calculations show that this assumption may be incorrect and experimental data on CF₃COF indicate that electron diffraction data carry information about the interdependence.