

Gas Electron Diffraction

Recent Problems in Diffraction by Gases

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The developments in diffraction by gases in the thirty years since the inception of the method have made it a powerful method for studying nuclear configuration and motion in gaseous molecules. Further developments are needed in the treatment of complex atomic scattering and in the precision of the experimental data.

The application of electron diffraction to molecules in the gaseous state for the purpose of obtaining structural information is now thirty years old¹. The developments during that period have provided techniques for obtaining fairly precise information on internuclear distances related to the equilibrium configuration of the molecule, on the mean amplitudes of the thermal motions and in some cases on the non-harmonic motions related to asymmetric vibrations or to internal rotations and also on the potential field acting between parts of the molecule². These possibilities have been utilized in obtaining fundamental information on a considerable number of molecules, and the methods have been sufficiently explored that it should now be possible to prescribe a more or less standardized procedure whereby principal attention could be given to the study of many more molecules having structural chemical interest and less attention to procedural developments. The following remarks are pertinent to the establishing of a standardized procedure.

It has become fairly usual now to consider an intensity function of the sort:

$$M \equiv \frac{I-B}{B} \quad (1)$$

where I represents the total intensity of scattered electrons and B represents that part of the scattered electrons which is dependent only on the number and chemical identity of the atoms in the molecule, and includes the coherent and non-coherent effects of the independent atoms (as well as the extraneous scattering when experimental values of M are considered). The numerator repre-

sents the structure-dependent part of the total scattering. The use of this relative intensity expression has the great advantage of cancelling out the rapid decrease in the intensity with increasing scattering angle as well as the dependence on the sector opening in the almost universally used rotating sector technique.

The theoretical value for M is as follows:

$$M(\text{theor}) = \frac{\sum |f_i| |f_j| \cos(\eta_i - \eta_j)}{\sum \{ |f_i|^2 + g_i \}} \times \int_0^\infty P_{ij}(r) \frac{\sin sr}{sr} dr \quad (2)$$

where the complex character of the atomic scattering factors is recognized, and the structurally interesting functions $P_{ij}(r)$ are to be obtained by analysis of experimental data for M . In some methods of analysis it is useful to modify M so that $P_{ij}(r)$ represents only the internuclear separations and does not depend on the electron distribution in the atoms. This can be accomplished by applying an additive correction, ΔM , which is similar in form to M but with the coefficient of the integral given by

$$\left\{ \frac{Z_i Z_j}{\sum (Z_i^2 + Z_i)} - \frac{|f_i| |f_j|}{\sum (f_i^2 + g_i)} \right\} \cos(\eta_i - \eta_j) \quad (3)$$

The corrected M with Z 's in place of f 's represents the molecular scattering corrected for non-nuclear effects and is in fact equal to the actual molecular scattering at larger angles (i.e., the coefficient in ΔM reaches zero at moderate s values). The corrected M is not equal to the scattering by the equivalent assemblage of bare nuclei even at large angles as can be shown by comparing the $(\eta_i - \eta_j)$ values for neutral atoms³ with

the corresponding phase differences for bare nuclei⁴).

An interpretation of the experimental M data has often been used in the form:

$$G(r) \equiv \int_0^{\infty} s M_{\text{corr}}(\text{exp}) \sin sr ds \quad (4)$$

where suitable allowance is made for the limited range of the data. If the factors $\cos(\eta_i - \eta_j)$ are approximately equal to unity, then $G(r)$ presents a simple function of the internuclear distance distributions,

$$G(r) \sim \sum Z_i Z_j \frac{P_{ij}(r)}{r_{ij}} \quad (5)$$

This radial distribution function is particularly satisfying in providing one peak for each internuclear distance, where the shape of the resolved peaks immediately indicates the behaviour of the internuclear motion; equilibrium distances and mean amplitudes are readily deduced from the symmetrical peaks which have been observed in most cases.

This nice interpretation of $G(r)$ in terms of the $P_{ij}(r)$ is lost when $\eta_i - \eta_j \neq 0$. It was recognized by Schomaker and Glauber⁵ that two peaks appear in $G(r)$ for each internuclear distance when η_i and η_j belong to atoms with greatly differing atomic numbers; as the difference in Z 's becomes less, the two peaks gradually merge including a stage in which they appear as one peak with an abnormal spread affecting the apparent vibrational amplitude. Bonham⁶ has obtained an explicit expression for the dependence of $G(r)$ on r , using analytical functions for the dependence of η on Z and s and the assumption that $P(r)$ is Gaussian. Some clever mathematician may earn our gratitude by devising a similar expression without the latter assumption, whereby an appropriate fitting of the experimental $G(r)$ would yield more complete information on the nuclear motions.

We have attempted several schemes of analyzing the data so that $G(r)$ can still be interpreted in terms of one peak per interatomic distance. For CH_3Br and CH_3I and their fluorine-substituted derivatives we modified expression (3) above so that the cosine factor applied only to the second term. The resulting ΔM is not necessarily small in any angular range; and while the "corrected"

$M(\text{exp})$ does then lead to equation (5), the procedure has been described as "substituting what you want for what you have". Still, the results obtained are objective as long as they are held to a strict consistency with the parameters assumed in the computing of the ΔM ; but this procedure can be satisfactory only when the number of structural parameters is quite small. A more common scheme when $Z_i - Z_j \leq 10$ is to calculate ΔM with expression (3) and then in the interpretation of $G(r)$ according to equation (5) to correct the apparent vibrational amplitude for the effect of the phase difference (as well as for the effect of any damping factor included in equation (4)). The general result of acknowledging the complex character of the atom factors is a complicating of the interpretive procedures especially in the so-called radial distribution method.

The impact of high speed computing methods has been considerable, and programs have been written for refining the raw data, for computing theoretical intensities and distribution functions, for resolving distribution functions into a specified number of components, for fitting theoretical and experimental functions and for other related uses. Not only has the greater convenience allowed stricter criteria to be applied in considering molecular models, but in some respects the precision of the results can be much better defined. The trend now is to fit either the experimental intensity or a distribution function with a theoretical function in a computing program which adjusts the molecular parameters according to a least-squares or other defined criterion. This leads to the warning and the hope that electron diffractoneers will not follow some other disciplines in confusing the precision of the results with the precision of the method of interpretation.

An example of the temptation was found in our current study of CH_3COCl where a radial distribution peak for the two bonded distances C-H and C=O was fitted with a maximum deviation of 0.1% and a r.m.s. deviation of 0.05% of the amplitude of the peak. The distance parameters delivered by the program were 1.133 and 1.187Å, the first being unacceptably high by 2 or 3% for the

bonds in a methyl group. Re-checking and re-testing the computing program exposed no fault, nor did a re-examination of the criteria for the satisfactory choice of the background in obtaining the experimental M function. Finally, it was discovered that the rotating sector had been damaged in a fashion which introduced variations in the observed intensity that were interpreted as related to the molecular scattering, i.e., the I function was in error by amounts far larger than represented by the precision of successful fitting with adjustable parameters.

While this example is extreme, it emphasizes my opinion that the precision of interpretation has outrun the precision of the experimental data and that the next real improvements must come in the precision of experimental data. The precision of I may be estimated as related to its reproducibility from one microphotometer tracing to another and from one negative to another; that of B is dependent upon the definition of a "smooth" background and upon the strictness of the

non-negative and zero limitations imposed upon the $G(r)$ function: the derived uncertainty in M is often many times that in I and B .

The establishment of a standard interpretive procedure yielding highly precise molecular parameters requires a re-consideration of the virtues of the "radial distribution" function and a careful consideration of the uncertainties in I and B and their effect on the reported parameters. No standard procedure can be applied in an automatic fashion with a guaranteed precision.

References

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- 2 The possibility of structural studies for electronically excited states should also be noted; cf. J. Karle, *J. Chem. Phys.* **35** (1961) 963.
- 3 B. K. Vainshtein and J. A. Ibers: *Electron Diffraction Tables in International Tables for X-Ray Crystallography*, Volume III.
- 4 N. F. Mott and H. S. W. Massey: *Theory of Atomic Collisions*, (Clarendon Press, Oxford) (1933) 35.
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- 6 R. A. Bonham and T. Ukaji: *J. Chem. Phys.* **36** (1962) 72.

DISCUSSION

J. KAKINOKI: What do you think about the accuracy in determining the interatomic distance? Is it 0.1% or 0.01%? Even when the diameter of the outmost halo is 100 mm, the accuracy of 0.1% means to measure the deviation of 0.1 mm on the photograph, and 0.01% means to measure that of 0.01 mm on it. This is very difficult even in the case of sharp Debye rings.

L. O. BROCKWAY: In my opinion the most favorable cases can now achieve 0.1% but not 0.01%. When several structural parameters are involved in the molecule, several different combinations of values may lead to agreement with the experimental data within the known precision of the data with the result of less than 0.1% accuracy—much less for parameters associated with a small part of the scattering power of the molecule. The reporting of errors in molecules of several parameters still needs some convenient way of showing the interrelations among the associated uncertainties.

K. HEDBERG: With respect to the necessity for caution in reporting results to high accuracy, particularly in the case of many parameter problems, suggested by Prof. Brockway; the use of least-squares refinement based upon intensity curves provides information about error correlation among parameters. I agree with Prof. Brockway; I suggest that the use of the least-squares method, together with consideration of the origin of errors not reflected in the least-squares results, is the proper way to handle this problem.

L. S. BARTELL: Regarding Prof. Brockway's not very optimistic conjectures about the accuracy of electron diffraction intensities as determined in current work, at present there is only one way to resolve this question, and that is to resort to experiment using molecules of known structure. Several papers to be given later in the conference present experimental data for diatomic and simple polyatomic molecules for which the spectroscopic structures are complete and unequivocal. In these cases observed errors in diffraction data agree well with errors estimated from the internal consistency of the diffraction experiments. Therefore I am optimistic that uncertainties as low as 0.001A can be (and have been) attained in careful work with present techniques.