International Union of Crystallography
Commission on Electron Diffraction.

Guide for the Publication of Experimental Gas-Phase Electron Diffraction Data and Derived Structural Results in the Primary Literature*

BY L. S. BARTELL, Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109, U.S.A, KOZO KUCHITSU, Department of Chemistry, Faculty of Science, The University of Tokyo, 3–1 Hongo 7–chome, Bunkyo-ku, Tokyo 113, Japan and H. M. SEIP, Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

(Received 2 December 1975; accepted 26 April 1976)

This report contains general recommendations for the guidance of authors, referees, and editors on the reporting of electron diffraction data and derived structures. They are intended to facilitate reliable evaluation, ease of comparison with other data, and the retrieval of information if later reanalysis becomes desirable in the light of new theories or experiments.

Introduction

This report is concerned with the presentation of structural investigations by electron diffraction. Its aim is to make results obtained by specialists more accessible to those in other disciplines and, at the same time, to increase the potential value of the original data to other specialists if subsequent events warrant reinvestigation. The needs of compilers and correlators of information will also be benefited by attention to these considerations. Only if enough information is provided to allow readers to appraise the precision and accuracy of the work, and only if reasonably uniform standards of reporting the results are adhered to, can all ends be met.


* This report is based on a draft written in 1973 by the Gas-Diffraction subcommittee of the IUCr Commission on Electron Diffraction in consultation with workers in a majority of the existing laboratories of electron diffraction. The present version incorporates suggestions received during discussions of the Guide in scheduled open sessions at the Austin Symposium on Molecular Structure, Austin, Texas, March, 1974; the Second European Crystallographic Meeting in Keszthely, Hungary, August, 1974; and the Tenth International Congress of Crystallography in Amsterdam, August, 1975; and by correspondence from interested IUCr members.

While an adequate documentation of experiment and interpretation is vital, so also, in the avalanche of scientific literature we must contend with, is brevity and conciseness. Possible ways to achieve both ends are as follows. It would be desirable to develop a compact style of reporting essential details that vary from analysis to analysis. Standard equipment and procedures in a given laboratory that have been described clearly in readily available journals or accessible depository services may be documented simply by citing the appropriate references. Workers in every laboratory have an obligation to provide this information, as outlined in the following sections and to revise it every few years when substantial changes are made. Special procedures and certain data that are important for a critical evaluation of results but not of general interest to readers should be summarized and placed in a suitable depository service or published as microfilm together with the article.

More and more highly specialized computer routines are being used to process data, to convert it to molecular parameters, to compute the effects of a host of influences such as electron density shifts, distortions of diffracted waves, molecular vibrations, etc., and to interpret derived structures in terms of quantum-chemical or other models. References to important computer packages employed and their sources should be given.

Structural investigations by gas-phase electron diffraction differ so much in complexity and in aim that it is impractical to recommend rigid rules for the reporting of procedures and presentation of results. Investigations in which low precision suffices need not be documented as minutely as those in which high precision is claimed. In the following are presented recommendations intended to be helpful in the preparation of a full paper. This guide may not fit all cases, and future developments may necessitate modifications. However, it is our hope that authors will deviate from the recommendations only after careful consideration.

I. Experimental apparatus and procedures

An adequate description of the experimental procedures used to obtain the numerical results should be made available. The major points to be considered are:
A. Sample
The source, verification of purity, and relevant handling procedures should be stated. When temperatures or reactivities are such that several species may be present, information concerning the vapor phase composition should be cited. The sample pressure should always be recorded when possible.

B. Reference to the diffraction unit used
If the detail of the unit has been published previously, a simple citation may suffice. If not, all relevant details must be given.

C. Uncertainty in the s-scale
The accuracy of measurement and means by which that accuracy is checked and maintained should be described.

D. Nozzle and sample temperature
The nozzle and reservoir temperatures are straightforward and should be reported. There is as yet no consensus on the effective temperatures of various internal molecular motions after the free expansion of the gas jet to the electron beam. Suitable caution in expressing the sample temperature seems advisable. The sample temperature at the electron beam depends upon (and, in principle, can be calculated from) the sample pressure, the nozzle dimensions, the distance of the electron beam from the nozzle lip, and the electron beam diameter. In all studies in which temperature is important, it is imperative that the above experimental quantities be given. Routinely the nozzle-beam dimensions should be made available.

E. Sector calibration (if used)
Some laboratories do and some do not calibrate the shapes of the sectors they use. It is important that an explicit statement be given about whether a calibration has been made, what means have been used, and what accuracy is achieved. A purely optical measurement with a standard traveling microscope may not be sufficient for the calibration of the inner range of a sector. For example, if the traveling microscope has a precision of $2 \times 10^{-4}$ cm and if a two parts per thousand precision in the sector opening is desired, the smallest radius of an $r^4$ sector that can be measured optically with the requisite accuracy is 1.1 cm for a sector with $r_{\text{max}} = 4.4$ cm and 1.8 cm for a sector with $r_{\text{max}} = 8.8$ cm.

F. Intensity measurement
The precision but not accuracy of the intensity measurements will be revealed, in part, in the least-squares residuals to be discussed later. Reference should be made to the calibration of the measuring device, both with respect to scattering angle and with respect to intensity value. Some laboratories favor establishing intensity measurement with reference to some standard molecule such as benzene. If photographic recording is used, the assumption of a linear density–exposure relation may distort derived amplitudes of vibration (or, in some cases, it may even interfere with the determination of structure). Whether plates are spun, oscillated (over what amplitude), or read with a linear scan should be stated.

G. Number of measurements
The number of independent data points used should be given (but see IID and IIDD below). If photographic recording is used, the numbers of plates for each camera geometry should be stated.

II. Treatment of diffraction data
In operations to transform observed intensity values into a form convenient for comparison with theoretical expressions, the major points to be enumerated are:

A. Leveling procedure
If intensities are leveled, converted to an $s^4 I(s)$ basis, or otherwise modified prior to determination of the background function, the requisite scattering factors or assumptions about electron distributions, polarization corrections, etc., should be identified.

B. Extraneous scattering corrections
Significant excursions of the background of leveled intensities from a flat, horizontal line should be noted. They may signify extraneous scattering (an additive effect), variation of plate sensitivity (a multiplicative effect) or inaccurate scattering factors. The manner of compensation can influence derived molecular parameters and needs to be known if later reanalyses of data are made.

C. Background function
The derivation of this important function (analytical or hand drawn) should be stated. It would be good practice to report the effective number of shape parameters implicit in the background if it has non-uniform derivatives.

D. Interpolation of data
The procedures used to interpolate and/or smooth data points and the means of determining data correlations should be referred to (see IID below).

III. Derivation of structural parameters

The principal points requiring attention are:

A. Equations relating intensities to molecular quantities
An explicit reference should be made to the electron scattering formulae used including scattering factors or electron distribution functions, polarization corrections, dynamic corrections, etc. Note that the functions adopted in structure refinements may not be the same as those employed in the leveling of data.

B. Auxiliary information
The values of force constants, rotational constants, or related quantities used in analyzing data should be given and their origin should be cited. Such quantities may enter the analysis in (1) computation of non-varied amplitudes of vibration; (2) computation of shrinkage corrections; (3) estimation of asymmetry parameters in internuclear distribution peaks; (4) searching for plausible models of refinement via the Westheimer–Hendrickson ‘molecular mechanics’ approach; (5) adopting spectroscopic quantities such as rotational constants as constraints or merging
them with diffraction intensities in the matrix of observations; (6) correcting spectroscopic quantities in (5) to be compatible with vibrational averages derived by diffraction.

C. Geometry adjustments

A discussion of the range of structural models tried must be given with statements: (1) whether symmetry constraints or other simplifications were imposed (e.g., assumptions of local Cs symmetry for a CFs group). All such constraints should be stated explicitly. (2) Whether multiple minima in least-squares solutions were searched for or encountered (false, deceptive minima are encountered in molecules as simple as SeO2F2). (3) Whether a static model with broadened peaks or a superposition of models distributed along various internal coordinates was taken.

D. Analysis of uncertainties

Estimates of the precision and probable accuracy should be given. It is essential to describe the various sources of uncertainty with a clear separation between measurement imprecisions, numerical analysis deviations, and possible systematic biases. The methods and assumptions made in the statistical analyses should be indicated including the weighting scheme and the inference of random errors and data correlations. Discussions of sources of experimental errors are given in several references, including Akishin, Rambidi & Spiridonov (1967); Bartell (1971); Bastiansen, Seip & Boggs (1971); Bauer (1970); Beagley (1973); Davis (1971); Harshbarger, Lee, Porter & Bauer (1969); Hilderbrandt & Bonham (1971); Karle (1973); Kuchitsu (1972a, b); Robiette (1973); Seip (1973); Vilkov (1964). Statistical analyses are outlined in several places including Bartell (1971); Bartell & Yow (1973); Bastiansen, Fritsch & Hedberg (1964); Hamilton (1964); Hedberg & Iwasaki (1964); Iwasaki, Fritsch & Hedberg (1964); MacGregor & Bohn (1971); Morino, Kuchitsu & Murata (1965); Murata & Morino (1966); Seip & Stølevik (1972); Seip, Strand & Stølevik (1969); Vilkov & Sadova (1967). One useful indicator that should always be determined and reported in diffraction studies is the 'index of pattern contrast' or 'index of resolution' defined as the ratio of \(I_{mole}(s)/I_{backg}(s)_{lab}\) to \(I_{mole}(s)/I_{backg}(s)_{true}\) best characterizing the adjustable scale factor for the molecular intensity in the strong part of the pattern. Values much lower than unity indicate a washed-out pattern or imperfect intensity calibration. In complex molecules with overlapping internuclear distances it may be prudent to investigate couplings between systematic errors in intensities and derived parameters over and above simple scale-factor errors (Bartell & Yow, 1973).

E. The meaning of the parameters determined

The physical significance of the lengths, angles, and amplitudes of vibration deduced is implicit in the form of the equation adopted to relate observations to derived quantities. The complexity of the possible range of corrections (see IIIA, IIIB, and IVB) makes it necessary to identify explicitly the meaning of the final values reported insofar as possible. Many of the problems encountered are discussed in Iijima (1972); Kuchitsu (1968); Kuchitsu & Cyvin (1972); Rambidi & Ezhov (1968); and Sutton (1965).

IV. Presentation of results

The most important considerations are:
their \( r_s \) values and bond angles and torsion angles are given the values in an \( r_e \) structure. In such an \( r_e \), structure, which can always be expressed in Cartesian coordinates in the case of acyclic molecules, internuclear distances differ from true mean distances only by relatively small 'Bastiansen–Morino shrinkage corrections'. A disadvantage of the \( r_e \) convention is that its basis is less fundamental in that it requires an arbitrary distinction between bonded and nonbonded distances. Furthermore, in the case of those cyclic molecules whose ring angles can be altered by a totally symmetric stretching deformation, the \( r_e \) structure cannot be precisely self-consistent (except by accident).

(2) Bond angles:

No special notation has arisen and none seems necessary at this time. It is well to mention, however, that angles deduced solely from \( r_s \) or \( r_e \) distances without shrinkage corrections in general cannot correspond exactly to angles in a geometrically self-consistent structure, and the difference between \( r_s \)-based angles and the self-consistent \( r_e \) angles may far exceed experimental uncertainties. When amplitudes of vibration are very large, the physical meaning of bond angles may be obscure, particularly in the case of quasilinear or quasiplanar molecules. Due caution in reporting should be exercised in these cases.

(3) Amplitudes of vibration:

These are commonly designated by the symbols \( l \) or \( u \), either of which is acceptable. For purposes of illustration we follow Cyvin (1968) and write \( l \):

\[
l_p = \left[ \int (r-r_s)^2 P(r) dr \right]^{1/2}
\]

\( l_e \) represents \( \left[ \int (r-r_e)^2 P(r) dr \right]^{1/2} \) where \( P(r) \) is the effective amplitude found by identifying the vibrational modulation of the molecular intensity curve with the damping factor \( \exp (-l_s r_s^2)/2) \).

(4) Interference patterns:

\( s \) The scattering variable \((4\pi/\lambda) \sin (\varphi/2)\) where \( \varphi \) is the scattering angle.

\( \kappa \) A parameter, characteristic of the asymmetry in an intermolecular distribution peak, showing up in the argument of the associated sinusoidal interference features as \( \sin (\kappa r - ks^2 + O(s^4)) \).

\( f(s), \eta(s) \) Complex atomic scattering factor for electrons where \( f(s) = f(s) \exp i\eta(s) \), assuming that atoms are spherical. Notation for corrections for atoms in molecular environments is not yet standardized.

C. Mode of presentation of the results

The CODATA Task Group (CODATA, 1973) recommends, as a general principle, that results be reported in a form as free from interpretation as possible (i.e. as close as is practical to experimentally observed quantities). These results should be reported in such a manner that the degree of experimental randomness can be assessed. The reader should be able to recover enough of the experimental data so that he can reanalyze them in terms of different hypotheses. Graphical and analytical representations of important results, although convenient for the reader, are not acceptable substitutes for tabular presentation of accurate experimental results.

D. Quantities to be reported in standard structure analyses

Publication of the following tabular and graphical information is recommended:

(1) Tables

(a) Digital values of leveled total intensities (molecular plus background) and the background used by the author. Alternatively, the molecular intensities might be substituted for the leveled total intensities (while retaining a report of the background). Molecular intensities are less 'primary' than total intensities but are more convenient to analyze. These vital data should always be made available in work meriting publication in standard professional journals but may be deposited as supplementary material rather than as a tabulation in the journal article itself. It would be desirable to report indices of resolution for the various camera geometries here as well as in the text.

(b) Bond distances, bond angles, and their uncertainties.

The meaning of the uncertainties must be specified in the tables as well as in the abstract and it is recommended that \( 2\sigma \) or \( 3\sigma \) be reported since they are more appropriate quantities than \( \sigma \) for consumption by non-specialists. Present methods of estimating \( \sigma \) are unreliable because errors are not statistically distributed in conventional diffraction analyses. It is to be hoped that progress will be made in error analyses.

The table should refer to a description of the principal systematic errors as well as random errors, either by direct inclusion, in a footnote of the table, or by an explicit reference in the table to the part of the text or other publication where the errors are discussed. The discussion should include how known systematic errors are corrected and how the magnitudes of poorly known systematic errors are estimated and included in the final uncertainties.

(c) Mean square amplitudes. The temperature should be specified insofar as is possible.

(d) Error matrix or correlation matrix for derived parameters (Hamilton, 1964). The correlation matrix with elements \( q_{ij} \) is more immediately diagnostic of potential troubles in the analysis (if correlations are high) than is the error matrix. The full error matrix with elements \( q_{ij} = \sigma_i \sigma_j \) is needed to calculate regression lines. The regression slope \( q_{ij} = \sigma_i \sigma_j \) may be valuable in allowing a quick estimation of \( D_{ij}/\Delta \theta_i \) where \( \Delta \theta_i \) is the expected change in parameter \( \theta_i \) from its least-squares value if subsequent information indicates that parameter \( \theta_i \) should be changed from its least-squares value by \( \Delta \theta_i \).

A good compromise between convenience and space is to tabulate the row matrix with elements \( \sigma_i \) and to tabulate immediately beneath it the correlation matrix. In some cases the correlation matrix is too large to warrant publication and a useful compromise might be to list only the elements with values exceeding, say, 0.5.

Some authors may wish to present a table of atomic coordinates to make it convenient for readers to calculate nonbonded distances, dependent angles, moments of inertia, etc. Interpretational difficulties (see IVB), however, may mar the utility of such a table.

(2) Figures

(a) Radial distribution curve. In many cases these curves and their residuals (the differences between experimental and calculated curves) provide insights not readily apparent in intensity curves. They should be labeled with clear indications of the assignments of the prominent features.

(b) Molecular intensity curves. It may be useful, particularly when the tabulated intensities are not published in the article itself, to illustrate the molecular intensity.
curves, including the residuals. These should never be considered as a replacement of the tabular information in IVD1a above, however, for such figures are not easily subjected to reanalysis.

Some authors may wish to present figures showing experimental and theoretical intensities for separate plates or separate camera geometries. In addition, figures may compare residuals with experimental uncertainties obtained by computing values from each plate separately. Such plots may often be helpful.

**Abbreviated check-list for electron diffraction publications**

I. Experimental apparatus and procedures
   A. Sample (source, purity, pressure)
   B. Apparatus (description)
   C. Uncertainty in the s-scale
   D. Nozzle specifications and sample temperature
   E. Sector calibration
   F. Intensity measurement
   G. Number of independent measurements

II. Treatment of diffraction data
   A. Leveling scheme (description if used)
   B. Extraneous scattering corrections (description if used)
   C. Background function (method of derivation, number of implicit shape parameters)
   D. Interpolation of data (procedures, smoothing involved, correlations in interpolated data)

III. Derivation of structural parameters
   A. Equations (scattering formulae, scattering factors)
   B. Auxiliary information (force constants, rotational constants, asymmetry parameters, etc.)
   C. Geometry adjustments
      1. Symmetry constraints imposed
      2. Whether multiple solutions searched for or encountered
      3. Method to represent peak broadenings
   D. Analysis of uncertainties (how done)

**References**


