

Significance of Bond Lengths Determined by Electron Diffraction*

L. S. BARTELL AND KOZO KUCHITSU**

*Department of Chemistry and Institute for Atomic Research
Iowa State University, Ames, Iowa, U.S.A.*

The derivation of structural parameters of known absolute significance, as mean and equilibrium bond lengths, from experimental electron diffraction patterns is discussed. A series of diatomic molecules has been investigated to test the theoretical interpretation of diffraction patterns, and, at the same time, to test the precision of the latest techniques of electron diffraction. Preliminary least squares results for bond lengths and amplitudes of vibration for the molecules O_2 , NO , N_2 , and Cl_2 , analyzed as Morse anharmonic oscillators, are reported. Standard errors range from $0.0008\text{\AA}$ to $0.003\text{\AA}$. The results, when corrected for vibrational effects, are found to agree with spectroscopic results to within experimental error. A brief discussion is given of the possible utility of the accuracy now attainable in structure determinations.

Introduction

The determination of precise internuclear distances in molecules is complicated by zero-point vibrations. The associated interpretational uncertainty, unless careful account is taken of vibrations, is of the magnitude of the "chemical shifts" in bond lengths from compound to compound, which it is of interest to measure. Such considerations have long been of concern in spectroscopy and have recently become important in electron diffraction owing to considerable improvements in technique. A critical test has never been made, however, of the absolute significance of electron diffraction structural parameters. Therefore we have undertaken a precise electron diffraction study of diatomic molecules to investigate the validity of current interpretational schemes.

Interpretation of diffraction data

A simple analysis of diffraction patterns, based on the equations of Debye's electron scattering theory¹⁾, has been presented for the derivation of experimental mean and equilibrium bond lengths of Morse anharmonic oscillators²⁾. Recently, somewhat more precise and general equations were derived³⁾ which are of particular utility when amplitudes of vibration are large.

The length most directly yielded by electron diffraction is the center of gravity, $r_g(1)$ of the experimental radial distribution peak, $f(r)$. For a Morse oscillator in its ground state it can be shown that the mean bond length, r_g , and equilibrium length, r_e , are very nearly

$$r_g \simeq r_g(1) + l_g^2/r_e$$

and

$$r_e \simeq r_g(1) + l_g^2/r_e - 3al_g^2/2 - \delta r_{\text{rot}}$$

where a is the Morse asymmetry constant. The terms l_g^2/r_e and $3al_g^2/2$ represent harmonic and anharmonic corrections, respectively. Amplitudes (rms) of vibration, l_g and l_e , reckoned from mean and equilibrium position⁴⁾, can also be derived by curve fitting $f(r)$ if a is known. While a can be derived by diffraction in favorable cases⁵⁾, it was calculated from vibrational spectra for the diatomic molecules discussed below.

Results

The molecules N_2 , NO , O_2 , and Cl_2 were investigated using the new electron diffraction unit at Iowa State University. Intensity measurements were restricted in angle to $s(\text{max})=58$ because of limitations in the travel of the microphotometer available. Wide angle Cl_2 plates were not taken and intensity data extended only to $s=41$. In all cases diffraction features were plainly apparent out to the edge of the region measured.

The results of preliminary least squares analyses of the experimental $f(r)$ curves are

* Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

** Present address: Department of Chemistry, Faculty of Science, The University of Tokyo, Tokyo, Japan.

Table I. Structural Parameters and Standard Errors.

parameter (Å)	O ₂	NO	N ₂	Cl ₂
$r_g(\text{e.d.})$	1.212 ₆	1.155 ₂	1.102 ₄	1.991
$r_e(\text{e.d.})$	1.207 ₃	1.150 ₃	1.099 ₀	1.983
$\sigma(r)$	0.001 ₁	0.000 ₃	0.001 ₇	0.002 ₅
$r_e(\text{spec})$	1.2074	1.1507	1.0976	1.988
$l_e(\text{e.d.})$	0.038 ₉	0.034 ₇	0.030 ₉	0.044 ₆
$\sigma(l)$	0.001 ₄	0.001 ₁	0.002 ₀	0.002 ₉
$l_e(\text{spec})$	0.0370	0.0349	0.0323	0.0462

listed in Table I and compared with spectroscopic values⁽⁶⁾.

Spectroscopic amplitudes were calculated for 300°K. Standard errors were computed from estimated scale factor errors (~0.6 ppt), indicated least-squares uncertainties, and in the case of amplitudes, certain uncertainties involving index of resolution (here nearly unity). No provision was made for errors in approximations of electron scattering theory.

Discussion

The close agreements in Table I lend weight to the present interpretation of the absolute significance of the diffraction parameters. Diffraction results for polyatomic molecules are as readily interpretable as those for diatomic molecules, and precise mean distances may be derived even if no data are available on the asymmetry constants. By contrast, the interpretation of spectroscopic results for polyatomic molecules

in terms of parameters of well understood absolute significance, is exceedingly difficult. Thus the simplicity of interpretation of diffraction results in comparison with spectroscopic results compensates appreciably for the intrinsically lower accuracy of the raw experimental data of diffraction.

The attainment of accuracy to 0.001Å by a method in which isotopic species can be studied independently promises to be helpful in studies of intramolecular force fields. Nonbonded interactions, which should alter internuclear distances, should be sensitive to amplitudes of vibration. Amplitudes in turn, can be varied by isotopic substitution. Studies are now under way to investigate such effects in hydrides.

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References

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DISCUSSION

D. A. SWICK: How, and with what accuracy do you measure your high voltage and camera distance?

L. S. BARTELL: We measure the high voltage in the same way Prof. Brockway has been doing it for nearly 30 years. We tap off a known fraction of the total voltage by means of a bleeder resistance consisting of precision wire-wound resistors, and measure it with a type *K* or similar potentiometer.

The camera distance, for a given nozzle position, is fixed by a carefully machined flange against which the emulsion surfaces of the plates are pressed during exposures. It is remarkably constant from plate to plate as measured with a traveling microscope.

We can measure the electron wave length and camera distance to about 3 parts in 10,000, as I recall.

L. O. BROCKWAY: I admire and respect the work of Prof. Bartell and agree that the question of precision of results should first be dealt with in cases where there are no molecular shape parameters involved. The precision reported here is of course not to be quoted as generally representative of electron diffraction work in the case of even

moderately more complicated molecules. Many problems of chemical interest can be discussed with results reliable to $0.005\text{\AA}$, and it seems certain that this can be achieved at least for the distances representing the larger contributions to the scattering power of the molecule.

Y. MORINO: The quantities which we obtain by the measurement are the diffraction intensities, but not the radial distribution curve. Therefore we must carry out the least squares calculation to make the deviation in the intensity minimum, not in the radial distribution function.

K. HEDBERG: Use of least squares with electron diffraction intensity curves always seems to lead to intuitively reasonable standard errors. In cases of simple molecules the errors are small; in complicated molecules they are larger. In those cases where radial distribution peaks are composite, the standard errors of both mean amplitudes and distances are large and highly correlated, as would be expected.

O. BASTIANSEN: I am not too pessimistic as to the accuracy of distance determination in more complicated molecules. I believe that our work indicates that even in more complicated molecules we may count on an accuracy of the same order of magnitude as in diatomic molecules.

S. H. BAUER: Can we distinguish experimentally the effects on the diffraction pattern between non-spherical electron distributions and anharmonic vibration?

L. S. BARTELL: Yes, I believe so. The effect of planetary electrons occurs almost entirely at small scattering angles where the quantity $[Z-F(s)]$ differs appreciably from Z . On the other hand, the effect of anharmonicity, as shown in the next paper in this program, occurs at large scattering angles. While effects of anharmonic vibrations have been observed recently, it is doubtful whether non-spherical properties of electron distribution would be detected with present electron diffraction technique.

DISCUSSION