Small-angle Scattering from Methane, Ammonia and Water by Fast Electrons[†,*]

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With the advent of improved methods for the calculation of the wave functions for a many-electron system, it has become of interest to obtain experimental measurements of quantities with direct relationships to the computed wave functions. Scattering experiments with fast electrons are of interest in this connection, since they provide direct information concerning the shape of electron-charge distributions in atoms and molecules.[1-8]

Some one-center wave functions, which are now available for the molecular systems methane, ammonia and water[9,10] have been

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used to calculate the total scattering intensity for fast electrons in the first Born approximation.[4,6] When these results are compared with those of the independent-atom model, a contribution from the binding electrons is seen to appear on the first ring of scattered intensities. This last calculation may be performed using the best available wave functions for each atom in these molecules. It is therefore, the purpose of this work to compare recently-obtained experimental results with these theoretical predictions.

Sector electron-diffraction photographs of methane, ammonia, water and helium were obtained over the s ($s=(4\pi/\lambda)\sin\theta/2$) range $1<s<8$ using a newly-constructed electron-fraction unit, in the Electron Diffraction Laboratory of Indiana University; this unit, to be described elsewhere,[11] has a nozzle-to-photographic plate distance of 65 cm. and an accelerating voltage of 40 kV. The diffraction patterns were recorded on Kodak process plates with an exposure time ranging from 1 to 3 min. and with a beam current of about 0.1 μ amp. The sample pressure was nearly 80 mmHg (except in the case of water, for which the pressure was $\sim$20 mmHg); the gas was expanded into the vacuum chamber through an orifice 0.15 mm. in diameter. The chamber pressure was maintained at better than 2×10^{-4} mmHg during the entire exposure time by the use of a fast pumping system. The optical density of the plates as a function of the scattering angle was measured using a newly-constructed automatic recording densitometer.[12]

The optical density measurements were made with a precision of better than $\pm0.5\%$; the s scale was also determined with a precision better than $\pm0.5\%$ at a maximum s value ($s=8.0$). The maximum optical density on any given plate was on the order of 0.35, and the intensity of electrons striking the plate was assumed to be proportional to the optical density. The intensity of electrons on Kodak process plates characteristically exhibits a quadratic dependence on the optical density that is usually less than 10% of the linear term. The recognition of this fact, coupled with the use of a sector correction based on helium to correct the experimental intensities, further compensates for the lack of an emulsion correction. Calculations showed that, for a nonlinear term of 10% in the optical density, an error of less than 2% was introduced into the experimentally-corrected intensities due to the neglect of the emulsion calibration.

The observed intensity curves were corrected for extraneous scattering by the use of a blank photograph taken under conditions identical with those encountered in the experiments. The helium experimental results were then matched, at $s=6$, with the best available theoretical results, using a single multiplicative scale factor. A wave function of the form:

$$\psi(\vec{r_1},\vec{r_2})=\{\exp[-Z_1r_1-Z_2r_2]+\exp[-Z_1r_2-Z_2r_1]\}\times(1+b\exp[-\alpha r_{12}])$$

was used to calculate the first Born-approximation elastic and inelastic scattering factors[13] employed in the calculation of the theoretical helium intensity. The parameters used in the above wave function were $Z_1=1.4079$, $Z_2=2.2085$, $b=-0.5780$ and $\alpha=0.2925$ (in atomic units). The total energy given by this wave function is 2.90188 Hartrees. The necessary expressions for the scattered intensity can all be obtained in terms of closed-form analytical functions. The ratio of the calculated to the observed helium intensities was then employed to correct the methane, ammonia and water intensities for uncertainties in the shape of the rotating sector, for magnetic disturbances from the sector-bearing, and for the lack of an emulsion calibration.

For the final analysis, the three best helium plates were selected in constructing the sector correction. The helium results are shown in Fig. 1. The best two plates each for methane, ammonia and water were selected; these results,

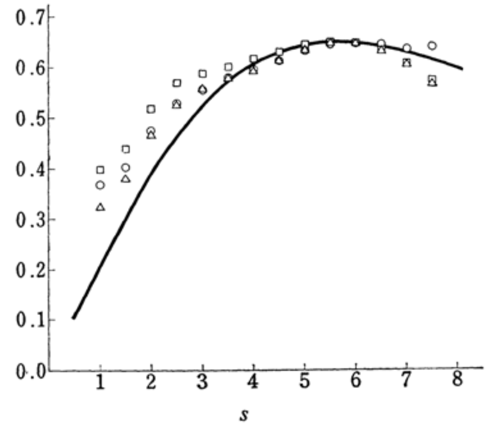

Fig. 1. Comparison of theoretical (——) and experimental (△, □, ○) intensities for atomic helium using an s^3 sector. The intensity scale is in arbitrary units. The theoretical and experimental curves are matched at $s=6$.

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[11] F. Momany, T. Iijima, D. A. Kohl, M. Williams and R. A. Bonham, to be published.

[12] D. A. Kohl and M. Williams, to be published.

[13] One of us (R.A.B.) wishes to thank the students in his advanced quantum mechanics class for calculating the analytical functions for the elastic and inelastic scattering factors used for the analysis of the helium intensity.

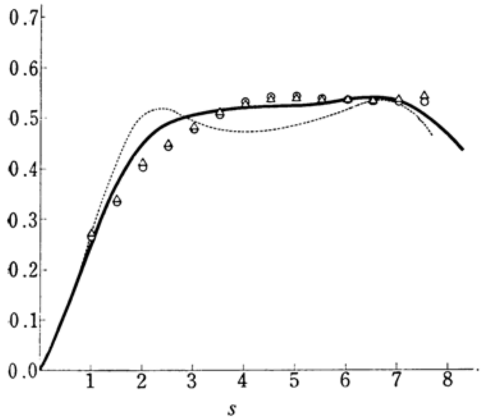

Fig. 2. Experimental and theoretical intensities for methane on an arbitrary intensity scale with results matched at $s=6$.

1. Experimental points : △, ○
2. Theory including binding effects ——
3. Independent-atom model ----

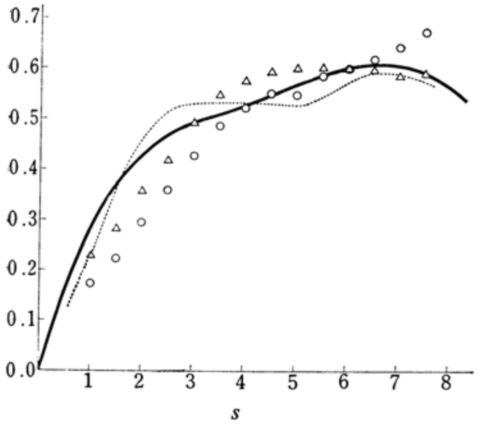

Fig. 3. Experimental and theoretical intensities for ammonia on an arbitrary intensity scale with results matched at $s=6$.

1. Experimental points : △, ○
2. Theory including binding effects ——
3. Independent-atom model ----

after having been sector-corrected, are compared with the theoretical results in Figs. 2, 3 and 4. The agreement with theory in the case of methane is quite gratifying. Unfortunately, the reproducibility of the ammonia and water results indicates only a general qualitative agreement with the theory.

The uncertainty in the present results possibly occurs because of extraneous scattering or intermolecular multiple scattering. Further improvement of the experimental conditions in order to reduce such effects is currently in progress. A further possible source of confusion is the neglect of polarization effects in the theoretical scattering calculations. There are also uncertainties involved in the comparison of theoretical and experimental results because of the approximate nature of the molecular wave functions used. This error should be at a maximum for water, while it should have its smallest value for methane.

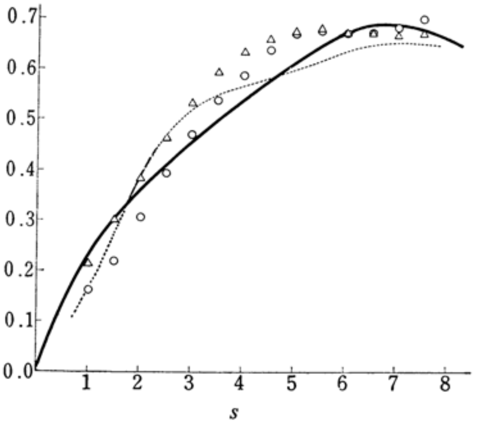

Fig. 4. Experimental and theoretical intensities for water on an arbitrary intensity scale with results matched at $s=6$.

1. Experimental points : △, ○
2. Theory including binding effects ——
3. Independent-atom model ----

In principle there are two effects associated with chemical-bond formation on the scattered intensity from polyatomic molecules. The first is the size effect, which is the main effect in the case of molecular hydrogen ; this has been discussed previously.[3,8] The size effect is essentially a change in the effective volume occupied by a fixed percentage of the electrons in the molecule when the independent-atom model goes over to the case where chemical bonds are formed. A comparison between the theoretical results for the independent-atom model and the experimental results or the theoretical calculation including chemical-binding effects shows that the formation of a stable molecular system is accompanied by a decrease in the volume occupied by a fixed percentage of the electrons.

The results of experiments on molecular hydrogen, reported elsewhere,[3,8] are essentially a measure of the effective volume occupied by a fixed percentage of the electrons in the molecule. This decrease indicates an increase in the kinetic energy over that of the independent-atom system ; hence, by the use of the virial theorem, it also indicates a lowering of the total energy. Because the independent-atom model represents the size and, thus, the total energy of the system without bond formation, the difference between this curve and the experimental curve is directly related to the binding energy of the system. Unfortunately, however, the total intensity is also related to the total number of electrons in the system, so the magnitude of the change between the independent-atom model and the experimental results will be proportional to the ratio of the number of electrons involved in the binding to the total number of electrons in the system. Thus the binding effects in systems containing large numbers of electrons, only a few of which are involved in chemical binding, will be quite small. This effect can also be observed in the differences, shown in Figs. 2, 3 and 4, between the independent-atom results (dotted curve) and the results including binding effects (solid curve). According to the simple ideas of valence theory; the magnitude of the binding effects for covalent bonds should be 8/10 for methane, 6/10 for ammonia and 4/10 for water, as compared with the effect in molecular hydrogen.[3,8] (A more detailed examination, appealing to electronegativity concepts, gives ratios slightly different from these.)

The second effect due to bonding arises because of the dipolar character of hetero-atom pairs. In the case of hetero-atoms, the scattering is sensitive to the shifts of charge from one atom to another which occur due to differences in the electronegativity of the atoms involved. This is especially significant in molecules possessing permanent dipole moments; it has been discussed previously by Altshuler.[14] The scattered intensity is proportional to $\mu^2/3s^2$, where μ is the permanent dipole moment, in the limit as s goes to zero. Unfortunately, this effect may tend to be obscured by polarization effects.

Since size effects and dipole effects occur together, it is of some interest to attempt to isolate one effect from the other. One possibility which suggests itself is to analyze the molecular wave function into "ionic" and "atomic" parts according to the scheme suggested by Shull.[15] In this fashion, the scattered intensity using the "atomic"-like wave function with and without ionic contributions could be calculated. The difference between these cases could then possibly be interpreted in terms of charge drifts due to electronegativity differences in the hetero-polar chemical bonds. Unfortunately, it is felt that both the experimental and theoretical results presented in the present analysis are too crude to allow any conclusions to be drawn regarding the dipole character of the scattering. At any rate, however, the foregoing remarks point out the desireability of obtaining quantitative theoretical relationships between size and dipole effects, on the one hand, and experimental measurements of a limited part of the differential scattering cross section, on the other.

Work is presently under way to obtain more precise measurements, both experimental and theoretical, of the type of scattering presented here so that more detailed comparisons may be made. While this type of experiment is somewhat limited in the kind of information that can be obtained about charge distributions, there are many other possibilities of the use of scattering techniques to obtain such information. Indeed, many of these possibilities have already been previously discussed in the literature.[16-19]

Summary

The total differential scattering cross sections for the 40 kV. electron from the methane, ammonia and water molecules obtained experimentally over the $1\leqslant s\leqslant 8$ s range have been compared with the theoretical results. Good agreement with the theoretical results have been obtained in the case of methane. In the cases of ammonia and water the results are in qualitative agreement with the theoretical predictions, but uncertainties in both the theory and experiment prevent a detailed comparison from being made in these cases.

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