A Relationship between the Binding Energy and the Scattering Intensity of Electrons from Gas Molecules

By Takao IIJIMA

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido

(Received August 3, 1965; in revised form November 24, 1965)

The effect of chemical bond formation on the scattering intensity has been investigated in several recent theoretical and experimental studies[1-8] of the scattering of fast electrons from gas molecules. The results of these studies have indicated that the intensity of electrons scattered by molecules shows a decrease, or at least a difference, from the calculated intensity based on *the independent atom model*[6] in the region of small scattering angles. This decrease in intensity has been attributed to a change in the effective volume occupied by a fixed percentage of electrons due to chemical binding, and thus qualitatively related to the binding energy of the system.[6-8] The present communication is intended to show that this decrease in intensity is directly and quantitatively related to the binding energy of the molecule. The theoretical prediction of the binding effect for the H_2 molecule[6] has been found to be consistent with this relationship. Also, a preliminary value of the binding energy of methane has been obtained by the use of the same relationship.

Tavard and Roux[4] have recently presented the following suggestive integral formula:

$$\left\langle \psi \left| \sum\sum_{i<j} \frac{Z_i Z_j}{r_{ij}} - \sum\sum_{i,\mu} \frac{Z_i}{r_{i\mu}} + \sum\sum_{\mu<\nu} \frac{1}{r_{\mu\nu}} \right| \psi \right\rangle = \frac{1}{\pi} \int ds[s^4 I^T(s) - \sum_i Z_i^2 - \sum_i Z_i] \quad (1)$$

where Z_i is the atomic number of the ith atom, and r_{ij}, $r_{i\mu}$, $r_{\mu\nu}$ are the nuclear-nuclear, nuclear-electron and electron-electron distances respectively. The electronic wave function of the system is denoted by ψ; s is the scattering parameter $(4\pi/\lambda)\sin(\theta/2)$, and $I^T(s)$ is the total intensity of electrons scattered by the system involved in the first Born approximation. By noting that the left-hand side of Eq. 1 is the potential energy and by using the virial theorem, the total molecular energy, E_M, may be related to the total intensity of the electrons scattered by the molecule $I_M{}^T(s)$ through the expression:

$$E_M = \frac{1}{2\pi} \int_0^\infty ds[s^4 I_M{}^T(s) - \sum_i Z_i^2 - \sum_i Z_i] \quad (2)$$

When all the internuclear distances, r_{ij}, are infinitely large, Eq. 1 is reduced to:

$$E_A = \frac{1}{2\pi} \int_0^\infty ds[s^4 I_A{}^T(s) - \sum_i Z_i^2 - \sum_i Z_i] \quad (3)$$

where E_A is the sum of the atomic energies and $I_A{}^T(s)$ is the atomic background. By subtracting Eq. 2 from 3, the binding energy, E_b, is obtained as:

$$E_b = \frac{1}{2\pi} \int_0^\infty ds[s^4 I_A{}^T(s) - s^4 I_M{}^T(s)] \quad (4)$$

1) C. Tavard, M. Rouault, M. Roux and M. Cornille, *J. Chem. Phys.*, **39**, 2390 (1963).
2) C. Tavard, *Cah. Phys.*, **17**, 165 (1963).
3) C. Tavard, M. Rouault, M. Roux and M. Cornille, *J. chim. phys.*, **61**, 1324, 1330 (1964).
4) C. Tavard and M. Roux, *Compt. rend.*, **260**, 4460, 4933 (1965).
5) J. Geiger, *Z. f. Physik*, **181**, 413 (1964).
6) R. A. Bonham and T. Iijima, *J. Phys. Chem.*, **67**, 2266, 2769 (1963).
7) R. A. Bonham and T. Iijima, *J. Chem. Phys.*, **42**, 2612 (1965).
8) T. Iijima, R. A. Bonham, C. Tavard, M. Roux and M. Cornille, This Bulletin, **38**, 1757 (1965).

This relationship can be rewritten in a more convenient form by using the intensity calculated by the independent atom model, $I_{IAM}{}^{T}(s)$:

$$E_b=\frac{1}{2\pi}\int_0^\infty ds[s^4I_{IAM}{}^{T}(s)-s^4I_M{}^{T}(s)] + \frac{1}{2\pi}\int_0^\infty ds[s^4I_A{}^{T}(s)-s^4I_{IAM}{}^{T}(s)] \quad (5)$$

The integrand of the first term corresponds to the decrease in intensity discussed earlier,[6-8] while the second integrand is simply the molecular term calculated by the independent atom model.*

For the H_2 molecule, the right-hand side of Eq. 5 was evaluated by the use of the $I_M{}^{T}(s)$ value which was calculated with the Weinbaum(ionic) wave function and reported previously.[6,7] Because the calculated $I_M{}^{T}(s)$ values were available only up to $s=10$, the integration of the first term had to be terminated at $s=10$. The second integration was evaluated with a simple analytical expression:

$$\frac{1}{2\pi}\int_0^\infty ds[s^4I_A{}^{T}-s^4I_{IAM}{}^{T}(s)] = -\frac{e^{-2D}}{D}\left[1+\frac{5}{8}D-\frac{3}{4}D^2-\frac{1}{6}D^3\right] \quad (6)$$

(D: the H-H distance)

for the case of H_2.[9] The first term amounted to 0.267 Ry (Rydberg), and the second term, to 0.002 Ry; thus total binding energy was calculated to be 0.269 Ry, while the binding energy of the Weinbaum(ionic) function is 0.296 Ry. The discrepancy may reasonably be understood as due to the termination error, which may be estimated to be 0.03 Ry by the graphical extrapolation of the $s^4(I_{IAM}{}^{T}-I_M{}^{T})$ curve.

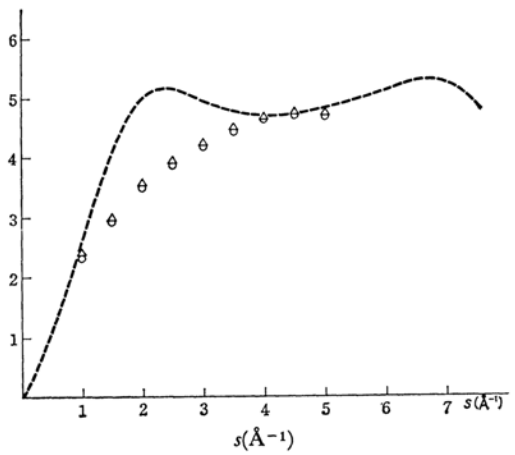

Fig. 1. The $s^3I_{IAM}{}^{T}(s)$ (--) and the observed scattering intensity with an s^3-sector of methane in an arbitrary scale. The results from two different plates are indicated by ○ and △. The difference in the scattering intensity shown in this figure which corresponds to the first integrand of Eq. 5, must be multiplied by s prior to integration.

The relationship given by Eq. 5 was used to analyze the diffraction data for methane** reported elsewhere.[8] Because of the lack of the sufficiently accurate experimental data in the region of large s values, there remains some ambiguity in the choice of a normalizing factor to make $I_M{}^{T}(s)$ fit the $I_{IAM}{}^{T}(s)$ intensity at large s values. On the assumption that no appreciable binding effect would appear in the range beyond $s=5$, the plausible normalization shown in Fig. 1 was made***; the intergration of Eq. 5 for this choice gave 1.06 Ry† as the binding energy of CH_4, a value which is in good agreement with the reported value of E_b, 1.34 Ry.[10] Both the first and the second term were integrated numerically.

It appears possible that a careful diffraction experiment could give the total binding energy of many molecules. This might be especially useful in cases where the determination of E_b by ordinary methods is difficult. Moreover, the known value of the binding energy might be used with the experimental intensity data to help provide estimates of such higher order effects on the scattering intensity as polarization and multiple scattering, by taking advantage of the relationship between the tatal intensity and the binding energy.

The author is greatly indebted to Professors Masao Kimura, Kimio Ohno, Kozo Kuchitsu and Russell A. Bonham, and also to Dr. Claude Tavard for reading the manuscript and giving helpful comments.

* The formulae equivalent to Eqs. 4 and 5 have also been obtained by Tavard; private communication via Professor R. A. Bonham; C. Tavard, to be published.

9) C. Tavard, private communication.

** The diffraction patterns for CH_4 were obtained in the Electron Diffraction Laboratory of Indiana University, Bloomington, Indiana. The author wishes to thank Professor R. A. Bonham for letting him use his apparatus.

*** The data beyond $s=5$, although not shown on the figure, are not in coincidence with the $s^3I_{IAM}{}^{T}$ curve. The inconsistency in this portion of data must be due to experimental error. A project to obtain more accurate intensity data is under way.

† The coherent and incoherent scattering factors used in the present calculation are based on the Hartree-Fock SCF wave functions.[11] Accordingly the value (1.37 Ry) thus obtained by Eq. 5 should be corrected for by the amount of the difference between the true atomic energy and the Hartree-Fock energy of carbon, namely, by about 0.31 Ry.[12,13]

10) G. Glockler, *J. Chem. Phys.*, **21**, 1242 (1953). The value reported by Glockler, 1.25 Ry, was corrected for the zero point energy by 0.09 Ry.

11) "International Tables for X-Ray Crystallogaphy," Vol. III, The Kynoch Press, Birmingham, England (1962).

12) C. E. Moore, "Atomic Energy Levels," National Bureau of Standards, USA (1949).

13) E. Clementi, *J. Chem. Phys.*, **38**, 996 (1963).