Electron Correlation and Binding Effects in Measured Electron-Scattering Cross Sections of CO_2

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Differential elastic high-energy electron-scattering cross sections for CO_2 have been measured and, with use of earlier total results, inelastic cross sections were derived. A comparison with the independent-atom model, molecular Hartree-Fock, and configuration-interaction calculations reveals the importance of the electron correlation for a first-order density property (elastic scattering) and a second-order one (inelastic scattering). Integral quantities such as the potential-energy differences ΔV_{ee}(exchange) and $\Delta V_{ne} + \Delta V_{ee}$(Coulomb) are determined. In addition, the first precise molecular structure of a molecule has been derived from only elastic data.

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The shortcomings of molecular Hartree-Fock (HF) calculations have led to large-scale configuration-interaction (CI) wave functions. It has been demonstrated repeatedly that electron-diffraction data can be collected with sufficient precision that the differences of the differential cross sections based on the two theoretical approaches are measurable. Until recently these comparisons were limited to a few cases. HF and CI (including all single and double excitations) wave functions were used to calculate elastic- and inelastic-scattering cross sections only for H_2,[1,2] some rare-gas atoms,[3] and a few small molecules.[4-7] The wave functions were squared to determine the charge density, Fourier transformed to compute the scattering factors for one specific molecular orientation, and finally orientationally averaged to predict the scattering amplitudes in the first Born approximation. While in the past the comparisons of molecular HF results with data showed significantly reduced deviations relative to the independent-atom model, the residuals were still several times larger than the experimental uncertainties.[8,9] The neglect of correlation in the theory was suspected as the cause of this disagreement. Final conclusions, however, were impossible because no scattering factors for molecules based on CI wave functions were available until very recently[5,6] (apart from the H_2 case[1,2]), and because the high-precision experiments did not energy analyze the scattered electrons, and thus the data included the sum of elastic- and inelastic-scattering intensities.

The result of several years of developments are presently coming to fruition simultaneously. A new experiment described below records the elastic and inelastic scattering separately without loss of the previously achieved precision. Furthermore, CI calculations[10] have been successfully completed for CO_2. These cross sections derived from the CI wave functions deviate significantly from equivalent results based on HF calculations. The comparison of the new experimental data with these theoretical results will demonstrate to what extent the binding and correlation effects are accounted for in the elastic and inelastic scattering, representing the first- and second-order density matrices.

A new electron diffraction unit has been designed and built. Most elements like the electron gun, the gas-handling system, the monitor, and the detector systems, including their electronics, are copies of our previous unit.[8] Essential changes have been made with regard to the vacuum pumps, the electron energy analyzer, and the angle-measurement device. The electron gun is mounted on a turntable, which is suspended on a 10-cm hollow shaft from the top. The shaft is connected to a large worm gear (33 cm) and ends with an incremental optical encoder with 2^{19}-bit resolution. This leads to an angular precision of 2 arc sec. The core of the shaft is utilized as the gas feeding line, terminating in a hypodermic needle. The vacuum chamber is evacuated with a 12-in. diffusion pump and an auxiliary 14-in. pump whose throat is extended through a large aluminum pipe into a cone with a 2-cm top opening. The hypodermic needle sits 1 cm above this opening in the center of rotation, discharging the target gas directly into the extended pump opening. Mounted on the wall of the vacuum vessel is a Moellenstedt electron analyzer. The design and the geometrical dimensions have been reproduced as given by Wellenstein.[11] The resolution was optimized at very small angles and the exit slit was opened to allow the whole elastic line to enter the detector system. With this slit setting, the scattering volume lies in the umbra of the detector's viewing field for the scattering angles reported here.

The diffraction unit, the alignment, and the calibration procedures will be described in full detail in a forthcoming publication.[12] The first gas investigated and reported here is CO_2. There are two reasons to choose CO_2. First, its bond length is used as a standard to calibrate the electron energy in gas-phase electron-diffraction studies. Second, new calculations of cross sections based on CI wave functions are available for comparison. In regard to the former there has never been a precision molecular-structure investigation based on purely elastic scattering. All former diffraction studies relied on the elimination of the inelastic scattering via theory and a smooth background function. This procedure is an approximation insofar as double-scattering processes involving consecutive elastic and inelastic interactions are neglected. The interference contribution to the elastic scattering can be depleted through this process. At present no intermolecular or intramolecular multiple-scattering theory takes this process into account. The data reported here were collected over an s $[=(4\pi/\lambda)\sin\theta/2]$ range of 1 to 10 a.u., where λ is the de Broglie wavelength of the incident electron and θ is the scattering angle. In order to avoid the binding effect, only data between $s=3$ and 10 a.u. were used in the structure analysis. Table I shows the final structure for CO_2 based on elastic and total data recorded in the same unit back to back. Because of the vibrational motion of the atoms in the molecule, electron diffraction does not determine the equilibrium structure, but a vibrationally averaged one.[14] It is very pleasing to see that the bond lengths did not vary within the stated uncertainties. These are assumed to be composed of two parts: 50% is contributed by the statistical uncertainty and 50% by the systematic errors. The mean amplitude of vibration for the C-O bond shows an increase, while the nonbonded value is well produced. The indices of resolution are very close to 1 and thus are not responsible for the shift in the root-mean-square amplitude of vibration, l(C-O). The elastic-inelastic intramolecular multiple scattering was expected to smear out the molecular interference pattern somewhat. The recording of purely elastic data removes in first order this perturbation and should have led to equivalent or smaller l values. Such multiple scattering would have explained the consistent disagreement of the l values based on previous experimental results and theory. Unfortunately, at present the purely elastic data cannot resolve this mystery. As for the future, precise data collection with a much larger s range is contemplated to continue the search for an agreement between the l values derived from spectroscopic and electron-diffraction data.

While the elastic data presented here are the first used in a structure determination, it is the binding and correlation effects which have been the primary motivation for these studies. It has been shown that the molecular binding can be investigated by precise electron-diffraction measurements. The scattering cross sections are not only sensitive to the basis sets used in the wave-function calculations[15] but also to correlation. Breitenstein and co-workers[5,6] have made *ab initio* calculations on the HF and CI level for several small molecules reaching up to 60% of the correlation energy. Since the change of the cross sections is only a few percent when compared with the independent-atom model (IAM) it has become common to present only the difference between the data and the IAM (delta sigma curve). Figure 1 shows this difference function for our elastic data and the IAM where HF partial-wave scattering factors have been utilized in the IAM. Since the data are relative only, the comparisons with theory are facilitated by matching over the large s range ($s > 5$ a.u.). The data were compared with two theoretical results. First, a difference curve of molecular HF and HF atoms is shown (dashed line). The agreement is already remarkable. This is a reflection of the fact that HF theory describes well all properties of the first-order density matrix and hence the elastic scattering.[16] A small change is introduced when the results of Breitenstein *et al.*[10] are used in the comparison (solid line). It is obvious from Fig. 1 that the CI calculations are in better agreement than the HF calculations. As in the case of N_2, the CI calculations[5] reduced the maximum at $s=4$ in accord with the data. The correlated elastic atomic scattering factors of Naon and Cornille[17] have not been used since they could not reproduce our Ne data which will be presented in a forthcoming detailed paper.[12] At present we can conclude that the elastic scattering is predicted quite well by the HF theory and excellently by the limited CI

TABLE I. Structure of CO_2 based on elastic and total scattering. The r's represent the molecular distances in angstroms, the l's represent the root mean square amplitudes of vibration in angstroms, R is called the index of resolution [it is introduced in the analysis to account for averaging effects due to the finite size of the scattering volume, detector apertures, etc. (Ref. 13)], and σ is the standard deviation between the final independent-atomic model (including a four-term polynomial for the unaccounted background) and the data.

Scattering	r(CO)	r(O · · ·O)	l(CO)	l(O · · ·O)	R	σ (%)
Total	1.1642(12)	2.325(4)	0.0336(70)	0.0468(70)	0.99(2)	0.27
Elastic	1.1649(10)	2.326(2)	0.0392(40)	0.0483(56)	1.01(2)	0.28

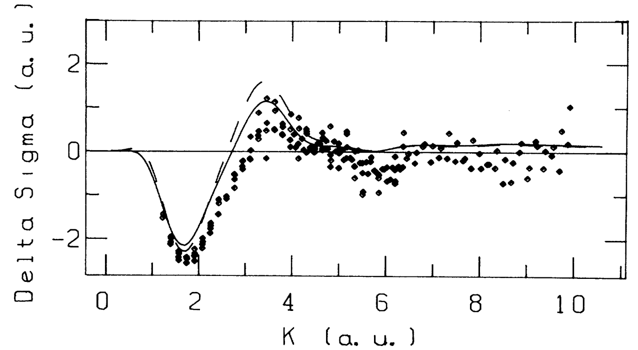

FIG. 1. CO_2 elastic delta sigma at 30 keV. Experiment, lozenges. HF theory, dashed line. Correlated theory, solid line.

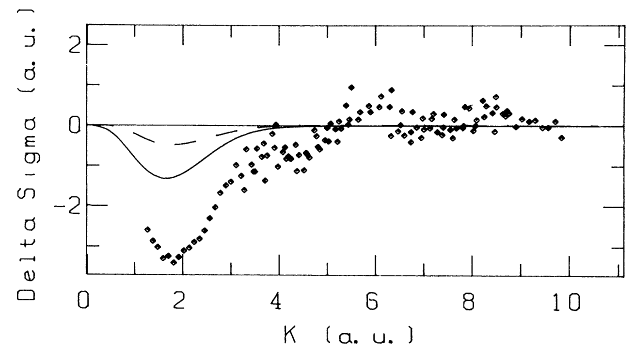

FIG. 2. CO_2 inelastic delta sigma at 30 keV. Experiment, lozenges. HF theory, dashed line. Correlated theory, solid line.

theory as developed by Breitenstein *et al.*[5]

Figure 2 depicts the differences of the inelastic cross sections $S(s)$ as a function of the momentum transfers when compared to various theoretical results. The elastic delta sigma was fitted by a high-order polynomial and this fit was used to subtract the elastic contribution from the total, which was taken from Fink and Schmiedekamp.[18] Direct subtraction would have needlessly overemphasized the counting noise. The inelastic portion of the data was referenced to the HF inelastic atomic scattering factors as calculated by Tavard, Nicolas, and Rouault.[19] In previous years the hope was nourished that the binding effect in $S(s)$ was insignificant, but the data of Duguet, on NH_3,[20] already raised severe doubts about this possibility, and these CO_2 data reconfirm the significant contribution of the binding in the inelastic-scattering cross section. As expected, HF theory is not able to predict the molecular inelastic scattering (dashed line). The limited CI theory (solid line) goes in the right direction, deepening the minimum at $s=2$ a.u. One could not hope that the CI calculations would agree with the data since only 40% of the correlation energy could be recovered in the computation. Upon following the scaling procedure[10] proposed previously for the comparison of experiment and theory, better agreement is found. The interpretation of the data is complicated insofar as the difference curves are composed of two effects; the atomic correlation and the molecular binding effects. Because of the shortcomings of the Naon-Cornille results a comparison with correlated atoms is not possible at present.

There are several interesting quantities in regard to the various potential energies where our data can be compared with HF and CI calculations. As was pointed out by Bonham and Fink[16] the following relationships hold:

$$V=V_{nn}+V_{ne}+V_{ee}=\frac{1}{4\pi}\int ds\, s^4\sigma_{\mathrm{tot}}(s)-\sum_{k=1}^{M}(Z_k^2-Z_k),$$

$$V_{nn}+V_{ne}+V_{ee}(\mathrm{Coulomb})=\frac{1}{4\pi}\int ds\, s^4\sigma_{\mathrm{el}}(s)-\sum_{k=1}^{M}Z_k^2,$$

$$V_{ee}^{nc}=V_{ee}(\mathrm{exchange})=V_{ee}-V_{ee}(\mathrm{Coulomb})=\frac{1}{4\pi}\int ds\, s^4\sigma_{\mathrm{inel}}(s)-\sum_{k=1}^{M}Z_k,$$

where

$$V_{nn}=\frac{1}{2}\sum_{i\neq j}^{M}\sum^{M}\frac{Z_iZ_j}{r_{ij}},\quad V_{ne}=-\sum Z_i\int\frac{dr\,\rho(r)}{|\mathbf{r}_i-\mathbf{r}|},\quad V_{ee}=\frac{1}{2}\int dr\frac{\rho_c(r)}{r},$$

$$V_{ee}(\mathrm{Coulomb})=\frac{1}{2}\int dr\,\rho(r)\int\frac{dr'\,\rho(r')}{|\mathbf{r}-\mathbf{r}'|},$$

M is the number of atoms in the molecule, the σ's are the differential cross sections, Z_i is the atomic number of the constituent atoms, $\rho(r)$ is the first-order density, and ρ_c is the second-order density. For detailed information concerning the potentials and the integral relationships, see Ref. 16.

The three integrals above, relating the scattering intensities with the potential energies, are not evaluated directly, since the breakdown of the first Born approximation would lead to erroneous results. This problem is avoided when first the differences between the measured results and partial-atomic-wave scattering-factor calculations are formed. The importance of the atomic scattering factors is discussed in Ref. 12. Then the above relations can be reformulated in terms of the potential differences, ΔV. This evaluation of the integrals above with our data and the Hartree-Fock independent-atom model lead to the following values: $\Delta V = -73$ eV ± 2, $\Delta V_{ne} + \Delta V_{ee}$(Coulomb) $= -27$ eV ± 2, and ΔV_{ee}(exchange) $= -47$ eV ± 2. (Note that the energies quoted in Ref. 18 are half of this ΔV due to the virial theorem.) Unfortunately these three equations are not independent and thus are not sufficient to determine all four types of potential-energy differences.

Some doubts have been raised in regard to the potential-energy differences derived from the integration of the difference cross sections shown in Figs. 1 and 2. A closer inspection of the graphs of Ref. 10 shows that the problem arises from the large-angle data. In view of the surprising differences obtained between calculated and measured results for the elastic difference cross sections at large values of the scattering parameter s, discussed above, the measured results for potential energies derived from the present elastic and previous total scattering measurements are in substantial disagreement with calculations.[10] This comparison leads to one of two conclusions—either there is some error in the theoretical calculations, or the assumptions made in normalizing previous relative experimental measurements by ourselves and others are seriously in error. Further work needs to be done to clarify this very important issue.

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