Theoretical Study of Potential-Energy Differences from High-Energy Electron Scattering Cross Sections of CO_2

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Configuration-interaction calculations of the differential high-energy electron-scattering cross sections of CO_2 have been performed in the first Born approximation leading to encouraging results for the total as well as the elastic and inelastic scattering, separately. A study of the potential-energy differences accessible from the cross-section curves by numerical integration points to a serious problem connected with the experimentally limited range of integration.

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In the field of high-energy electron scattering on gases, CO_2 is one of the experimentally best-investigated molecular systems. High-precision differential cross sections are available not only for total scattering[1-3] but also for elastic and inelastic scattering,[4] separately. Presently available theoretical results[3] suffer from the fact that the molecular wave function used is confined to the HF (Hartree-Fock) level of approximation. Recent cross-section calculations for other linear molecules[5,6] have established that electron correlation is of fundamental importance for producing results comparable to experimental ones. Below we present configuration-interaction (CI) calculations of the total, elastic, and inelastic cross sections for CO_2, thus allowing quantitative comparisons with experimental results. The study includes the calculation of various contributions to the potential binding energy which can be derived from cross sections, as well as the comparison of these energies with their experimental counterparts.

Throughout this work we consider difference functions obtained by subtracting the appropriate independent-atom–model (IAM)[7] cross sections from the molecular cross sections. The difference functions studied in this work are $\Delta\sigma_{\rm tot}(s)$, $\Delta\sigma_{\rm el}(s)$, and $\Delta\sigma_{\rm inel}(s)$, referring to total, elastic, and inelastic scattering, respectively. The cross sections are taken to be multiples of the Rutherford cross section, and s is the scattering variable connected with the scattering angle θ and the electron wavelength λ by $s=(4\pi/\lambda)\sin(\theta/2)$.

In the first Born approximation (assumed to be valid for 30–40-keV electrons scattering on CO_2) the integration of each type of $\Delta\sigma(s)$ curves leads to a specific potential-energy difference term[8,9]:

$$\Delta V_{ne}+\Delta V_{ee}=(1/\pi)\int_0^\infty \Delta\sigma_{\rm tot}(s)\,ds, \tag{1}$$

$$\Delta V_{ne}+\Delta V_{ee}^{\rm c}=(1/\pi)\int_0^\infty \Delta\sigma_{\rm el}(s)\,ds, \tag{2}$$

$$\Delta V_{ee}^{\rm nc}=(1/\pi)\int_0^\infty \Delta\sigma_{\rm inel}(s)\,ds. \tag{3}$$

ΔV_{ne} refers to the potential energy of the electron-nucleus attraction and ΔV_{ee} to the potential energy of the electron-electron repulsion based on the proper two-electron density. $\Delta V_{ee}^{\rm c}$ refers to the "classical" or "Coulomb" repulsion energy based on the product of one-electron densities instead of the proper two-electron density. By subtraction of $\Delta V_{ee}^{\rm c}$ from ΔV_{ee} the "nonclassical" or "exchange" repulsion-energy term $\Delta V_{ee}^{\rm nc}$ is obtained.

$\Delta\sigma_{\rm tot}(s)$ and $\Delta\sigma_{\rm el}(s)$ were calculated as previously described.[6] $\Delta\sigma_{\rm inel}(s)$ was obtained by subtracting $\Delta\sigma_{\rm el}(s)$ from $\Delta\sigma_{\rm tot}(s)$. The IAM cross sections were treated on the HF level of approximation[6] (thus allowing direct comparison of the theoretical with the experimental results of Refs. 2 and 4 to be made). The molecular approximate HF (AHF) calculations were performed with use of the GAUSS76 program[10] and a $(10s6p2d)/[5s4p2d]$ basis set[11] of Gaussian-type orbitals (GTOs). The AHF energy obtained for the experimental equilibrium geometry (CO: 1.160 Å[12]) lies 0.015 a.u. above the best AHF literature value.[13] It can be expected[6] that our calculated AHF $\Delta\sigma(s)$ curves are very close to the exact HF ones.

The AHF $\Delta\sigma(s)$ curves were improved by adding the appropriate electron correlation correction

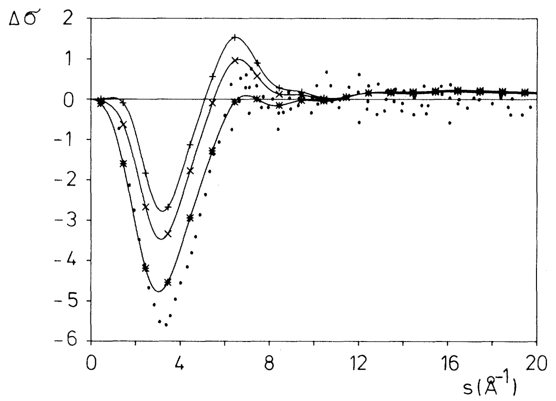

FIG. 1. $\Delta\sigma_{tot}(s)$ curves for CO_2. Pluses, AHF; crosses, AHF plus 4-31G +BF CI correlation correction; asterisks, AHF plus estimated full correlation corrections; dots, experimental.

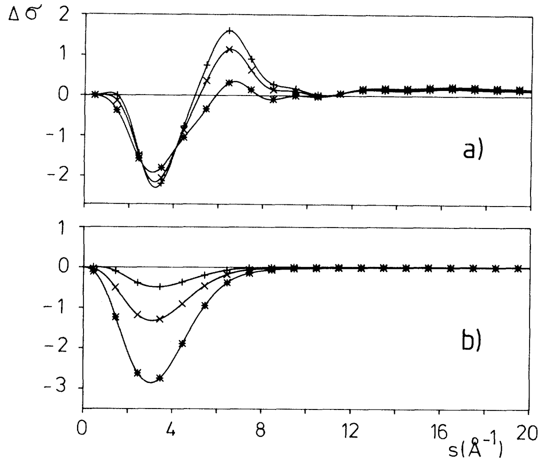

FIG. 2. (a) $\Delta\sigma_{el}(s)$ and (b) $\Delta\sigma_{inel}(s)$ curves for CO_2. Pluses, AHF; crosses, AHF plus 4-31G +BF CI correlation correction; asterisks, AHF plus estimated full correlation correction.

derived from a variational CI calculation including all singly and doubly excited configurations. The CI calculation was performed by use of the PERTCI program system.[14] Because of the limited computer facilities the CI calculations were made with use of a 4-31G + BF wave function.[15,16] From our experiences with similar calculations for smaller molecules we believe that the 4-31G + BF CI correlation correction terms are an acceptable approximation to more sophisticated ones.

The correlation energy obtained represents 40.5% of the empirical correlation energy, which we estimate to be −0.871 a.u., taking into account the AHF energy of Ref. 13, the nonrelativistic atomic energies of Veillard and Clementi,[17] and the experimental bonding and zero-point vibrational energies of Herzberg.[18,19] The potential part of the 4-31G + BF CI correlation energy covers 35.4% of the corresponding empirical value of −2.013 a.u. This energy was estimated by use of the virial quotient of a very extended AHF calculation.

According to the simple scaling procedure previously described[5,6] the full electron correlation correction to $\Delta\sigma_{tot}(s)$ may be estimated which represents the potential portion of the full empirical correlation energy. The scale factor to be applied to the correlation correction is $(35.4\%)^{-1} = 2.82$. The same value is used for the correlation corrections of $\Delta\sigma_{el}(s)$ and $\Delta\sigma_{inel}(s)$ separately.

Figure 1 displays the theoretical $\Delta\sigma_{tot}(s)$ curves obtained on the various levels of approximation together with the experimental result of Ref. 2. As expected the AHF curve (being quite similar to that of Ref. 3) differs most significantly from the experimental result. The marked shift of the outermost extrema to positive values is partly corrected when taking the electron correlation into account on the 4-31G + BF CI level of approximation. The best agreement with the experimental result, however, is achieved by including the estimated full correlation effect.[20]

In Figs. 2(a) and 2(b) theoretical curves corresponding to those of Fig. 1 are shown for the separate elastic and inelastic contributions to $\Delta\sigma_{tot}(s)$, respectively. The electron correlation corrections of $\Delta\sigma_{tot}(s)$, $\Delta\sigma_{el}(s)$ and $\Delta\sigma_{inel}(s)$, are displayed in Fig. 3. As it can be seen from these figures, the correlation effect removes the first low maximum of the AHF $\Delta\sigma_{el}(s)$ curve and flattens the characteristic consecutive extrema, the maximum being somewhat more affected than the minimum. The AHF $\Delta\sigma_{inel}(s)$ curve simply displays one flat minimum and this is strongly deepened by electron correlation. The correlation

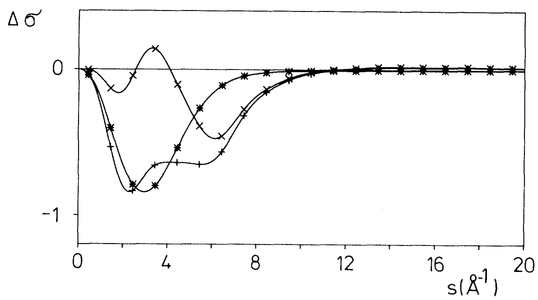

FIG. 3. 4-31G + BF CI correlation corrections in the $\Delta\sigma(s)$ curves for CO_2. Pluses, total; crosses, elastic; asterisks, inelastic.

TABLE I. Differences between the potential energies of the molecule and the IAM molecule (in electronvolts).[a]

Level of approximation[b]	s_u ($\mathrm{\AA}^{-1}$)	$\Delta V_{ne}+\Delta V_{ee}$	$\Delta V_{ne}+\Delta V_{ee}^{c}$	ΔV_{ee}^{nc}
AHF	∞	8.8	15.3	−6.5
AHF plus 4-31G+BF	∞	−10.6	10.0	−20.6
AHF plus empirical calculation	∞	−46.2	0.4	−46.6
	30	−53.4	−6.9	−46.5
	20	−60.8	−14.3	−46.5
	10	−68.3	−21.9	−46.4
Expt.[c]		-73 ± 2	-27 ± 2	-47 ± 2

[a] For $s_u\neq\infty$, obtained by numerical integration according to Eqs. (1) to (3); for $s_u=\infty$, directly computed (see text).

[b] Referred to the calculation of the molecule (the IAM molecule is always treated on the HF level).

[c] Ref. 4.

correction of $\Delta\sigma_{\mathrm{tot}}(s)$, i.e., the sum of the corrections of $\Delta\sigma_{\mathrm{el}}(s)$ and $\Delta\sigma_{\mathrm{inel}}(s)$, is dominated at small s values (up to $\sim 5\ \mathrm{\AA}^{-1}$) by the inelastic contribution, and at higher s values by the elastic contribution. Similar results were obtained for the other molecules studied so far.[5,6] In all these cases the elastic contribution turns out to be less pronounced than the inelastic one but *cannot be ignored when theoretical and experimental scattering cross sections are to be compared.*

In Ref. 4, experimental, $\Delta\sigma_{\mathrm{el}}(s)$ and $\Delta\sigma_{\mathrm{inel}}(s)$ curves for CO_2 are presented and compared in detail to our theoretical results. A note, however, is to be added here concerning the curves including the estimated full correlation effects which are not displayed in the figures of Ref. 4. The agreement of these curves with the experimental results is —compared to the 4-31G+BF CI curves—drastically improved in the inelastic case but slightly worsened in the elastic case. This is not too surprising in view of the crudeness of the simple scaling procedure applied. In fact, various CI calculations of increasing quality on smaller molecules suggest that the correlation correction term obtained by use of the scaling procedure is slightly overestimated in the elastic case and slightly underestimated in the inelastic case.[6] When we take this tendency into account, both estimated curves tend to even further approach their experimental counterparts.

Table I collects the theoretical and experimental data for the various potential-energy differences. The theoretical data are directly available from the AHF and CI calculations or—in order to mimic the experimental procedure—from numerical integration of the $\Delta\sigma(s)$ curves. In this context the important and nontrivial problem regarding the convergence of these integrals for $s_u\rightarrow\infty$ [s_u being the upper limit of the integral in Eqs. (1) to (3)] is addressed. Considering that the directly calculated results are identical to this limit, the numerical integrations are performed for values of s_u up to 30 $\mathrm{\AA}^{-1}$.

When going in Table I from one level of approximation to another (cf. rows 1 to 3) large changes occur in each type of potential-energy difference. Obviously, for the comparison with the experimental results the values including the full empirical correlation (row 3) should be the most appropriate ones. In fact, in the case of ΔV_{ee}^{nc} the agreement with the experimental value is very satisfactory. However, this is not the case for $\Delta V_{ne}+\Delta V_{ee}^{c}$ (and consequently for $\Delta V_{ne}+\Delta V_{ee}$, too). The essential reason for the disagreement must be seen in the relatively small range of integration available from experiment. Our investigations show (see rows 4 to 6) that the magnitude of $\Delta V_{ne}+\Delta V_{ee}^{c}$ is strongly influenced by the chosen value of s_u.

In view of the general expectation that high-energy electron scattering may constitute a promising tool for studying chemical binding effects it appears especially noteworthy that, for the representative case of $s_u=20\ \mathrm{\AA}^{-1}$, *the deviation between the integration result and the directly calculated value is of the same of order of magnitude as the total binding energy of* CO_2 *itself* (−17 eV). We expect that the integration limit problem connected with the experimental $\Delta\sigma_{\mathrm{el}}(s)$ curve—and likewise with the

$\Delta\sigma_{\mathrm{tot}}(s)$ curve—is not restricted to the example of CO_2 but will play a similarly important role for other molecules, too.

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[20] Note that the experimental data are adapted to the IAM data for larger values of s; if they were adapted to the present calculated molecular data the agreement could be even better.