

CI Calculations of X-ray Scattering Intensities for some Linear Molecules [1]

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X-ray scattering intensities for molecular gases have been calculated in the first Born approximation using correlated ab initio wavefunctions. The influence of electron correlation has systematically been studied for the series of molecules C_2H_2 , CO, N_2 , O_2 and F_2 . The correlation effects turn out to be very pronounced for the total and inelastic scattering and less so for the elastic scattering (where they cannot be neglected, however). Hopes are raised that the timely results will stimulate progress in the very recent research topic of gas X-ray diffraction.

Introduction

A recent gas X-ray diffraction study for CO_2 [2] raises hopes that measured X-ray scattering intensities will be soon available for other molecular gases, too. It is the intention of the present paper to stimulate experimental work by presenting calculated X-ray scattering intensities for some further molecules (C_2H_2 , CO, N_2 , O_2 and F_2). The calculations include molecular electron correlation effects since a recent study on CO_2 [3] has suggested that such effects are likely to play an important role for X-ray scattering intensities. The fundamental importance of electron correlation effects in the related field of high-energy electron scattering on gases [4–6] has been firmly established before.

Calculations

As it is commonly done our calculations are based on the first Born approximation and refer to the difference function $\Delta\sigma(s)$ between the molecular and the IAM (independent atom model) scattering intensities [7]; s is the scattering variable connected with the scattering angle θ and the X-ray wavelength λ through $s = (4\pi/\lambda) \sin(\theta/2)$. The computational details for obtaining the total scattering function $\Delta\sigma_{\text{tot}}(s)$ are the same as recently described for the corresponding electron scattering function [5]

considering, however, that the pure electron terms only have to be taken into account. The elastic contribution $\Delta\sigma_{\text{elast}}(s)$ to $\Delta\sigma_{\text{tot}}(s)$ was obtained in an analogous manner and the inelastic contribution $\Delta\sigma_{\text{inelast}}(s)$ as the difference of $\Delta\sigma_{\text{tot}}(s)$ and $\Delta\sigma_{\text{elast}}(s)$.

The IAM scattering intensities were evaluated on the HF (Hartree-Fock) level of approximation (following the usual procedure in experimental scattering work). The molecular scattering intensities were treated on three levels of approximation: AHF (approximate HF), AHF CI (configuration interaction) and AHF connected with a scaled estimate of the full correlation effect (thereafter denoted AHF scaled CI) [4, 5]. The total energies of the GTO (Gaussian type orbital) AHF calculations including two sets of d functions are near to the HF limit and the CI calculations performed with a selection of singly and doubly excited configurations represent about 50 to 60% of the potential energy portion of the full empirical correlation energy (for details of the calculations, see [5]).

Results and Discussion

The $\Delta\sigma_{\text{tot}}(s)$ and $\Delta\sigma_{\text{inelast}}(s)$ curves corresponding to the aforementioned three levels of approximation (AHF, AHF CI and AHF scaled CI) are displayed in Figs. 1 and 2, respectively. Table 1 lists values of the integrals

$$\Delta V_{\text{ee}} = \frac{1}{\pi} \int \Delta\sigma_{\text{tot}}(s) \, ds \quad (1)$$

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and

$$\Delta V_{ee}^{nc} = \frac{1}{\pi} \int \Delta \sigma_{inelast}(s) ds, \quad (2)$$

where ΔV_{ee} refers to the proper electron repulsion energy and ΔV_{ee}^{nc} to the “nonclassical” contribution [8, 9]. These values may be of interest for molecular binding energy analyses or, in particular, for an experimental examination by gas X-ray diffraction.

The AHF curves are in excellent agreement with the corresponding results for CO, N₂ and O₂ of [10]. Since these results were derived from STO (Slater type orbital) wavefunctions, which are very near to the HF limit, the good agreement confirms that our AHF scattering curves are nearly identical with the (unknown) exact HF $\Delta \sigma(s)$ curves.

An obvious feature of all AHF $\Delta \sigma_{tot}(s)$ curves (Fig. 1) is the first extremum: a marked maximum for C₂H₂, a much less pronounced maximum for CO and N₂ going over to a distinct minimum for O₂ and F₂. This effect is reflected in the corresponding values of ΔV_{ee} (Table 1). When going from C₂H₂ to F₂, i.e. from the left to the right in the periodic table of elements, the range of s values over which $\Delta \sigma_{tot}(s)$ assumes significant values is broadened, reflecting roughly – via Fourier transformation – the decreasing size of the corresponding atoms. It should be noted that the behaviour of the extremum described above is – qualitatively – just opposite to the behaviour found in the corresponding electron scattering curves [5].

The $\Delta \sigma_{inelast}(s)$ curves – which are equally valid for X-ray and electron scattering – are remarkably flat over the whole range of s values in the AHF case (Figure 2). Accordingly, the values of ΔV_{ee}^{nc} are only slightly negative (C₂H₂ and CO) or slightly positive (N₂, O₂ and F₂) (Table 1). Obviously – as stated before [10] – the AHF inelastic scattering of a molecule is very similar to that of its constituent atoms. As a further consequence the AHF $\Delta \sigma_{elast}(s)$ curves (not shown) are very similar to their AHF $\Delta \sigma_{tot}(s)$ counterparts.

The (molecular) AHF scaled CI electron correlation corrections for the total as well as the elastic and inelastic scattering functions are shown in Figure 3. The curves were obtained from the AHF CI results (not shown) using the scale factor method [4, 5] and may be considered to represent – via Tvard’s theorem [8] – the corresponding electron repulsion portion of the full electron correlation

energy. For CO, correlation corrections had been previously obtained [11] using a molecular wavefunction which included only 21% of the empirical correlation energy. Nevertheless, the qualitative features of these corrections are similar to those revealed by our more sophisticated calculations.

The correlation corrections of $\Delta \sigma_{tot}(s)$ are very similar in form (essentially characterized by a more or less deep minimum) for all molecules considered. The values of the corresponding integrals (multiplied by $1/\pi$) are unsystematically distributed between -0.4 au (N₂) and -1.2 au (F₂). In analogy to findings in high-energy electron scattering, electron correlation preponderantly affects the inelastic scattering; electron correlation effects on the elastic scattering (exhibiting a rather individual behaviour for the various molecules) are not negligible and should be included in future comparisons with experimental results.

Although all AHF $\Delta \sigma_{tot}(s)$ curves are comparably lowered when electron correlation is taken into account the final result looks quite different for the various molecules. Taking the scaled CI case, e.g., the total scattering curve of C₂H₂ is hardly affected; for CO and N₂ the characteristic maximum has almost disappeared and for O₂ and F₂ the minimum becomes much more accentuated. These results are clearly reflected in the corresponding energy values (Table 1).

In contrast to the total scattering curves, the correlation corrected inelastic scattering curves are very similar in form within the series of molecules considered (Fig. 2) and even the corresponding energy values show little variation (Table 1). How-

Table 1. Differences between the molecular and IAM electron repulsion energies ΔV_{ee} and ΔV_{ee}^{nc} (in au)^a.

Molecule	ΔV_{ee} electron correlation		ΔV_{ee}^{nc} electron correlation	
	excluded ^b	included ^c	excluded ^b	included ^c
C ₂ H ₂	1.73	1.30	-0.29	-1.02
CO	0.63	-0.22	-0.12	-0.96
N ₂	0.39	-0.01	0.07	-0.69
O ₂	-0.23	-1.19	0.05	-1.00
F ₂	-0.38	-1.58	0.05	-1.01

^a Calculated from (1) and (2) with an upper integration limit of $s = 10 \text{ \AA}^{-1}$.

^b Obtained from the AHF $\Delta \sigma(s)$ curves.

^c Obtained from the AHF scaled CI curves (i.e. with the scaled full electron correlation correction).

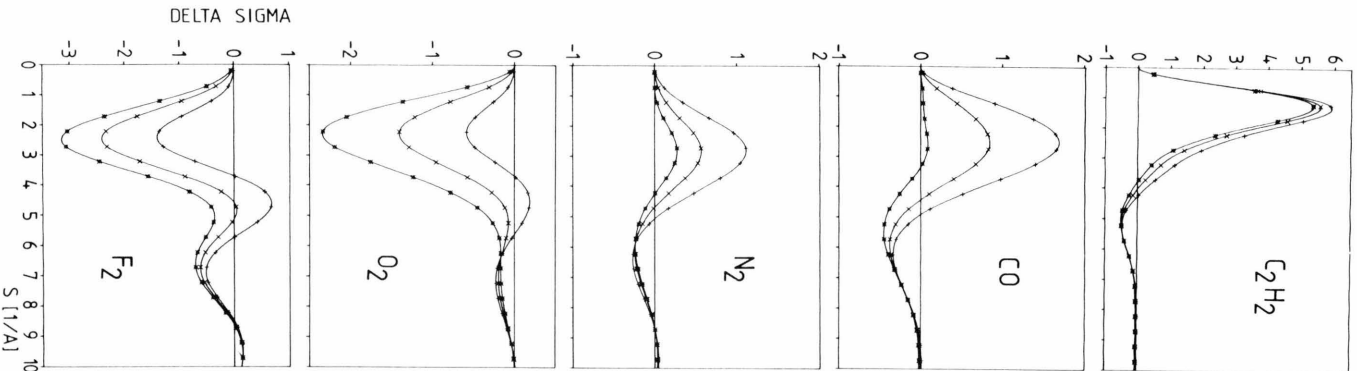


Fig. 1. $\Delta\sigma_{\text{tot}}(s)$ curves, + AHF; \times AHF CI; * AHF scaled CI.

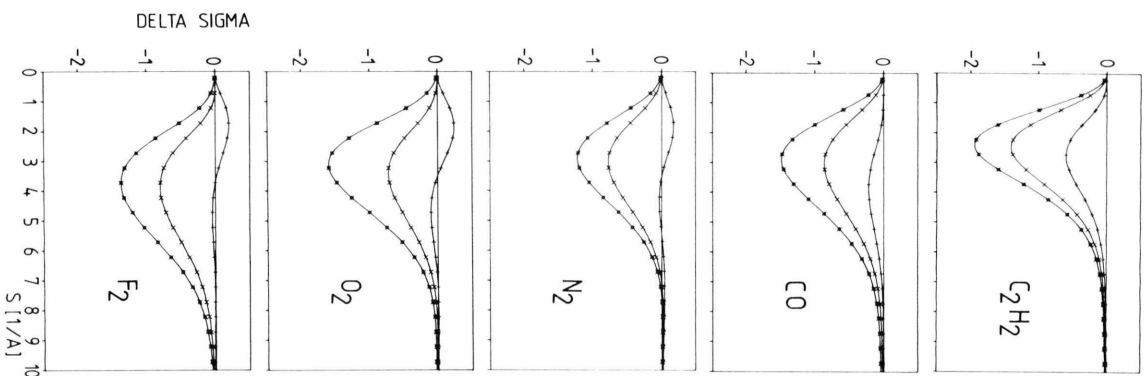


Fig. 2. $\Delta\sigma_{\text{inelast}}(s)$ curves, + AHF; \times AHF CI; * AHF scaled CI.

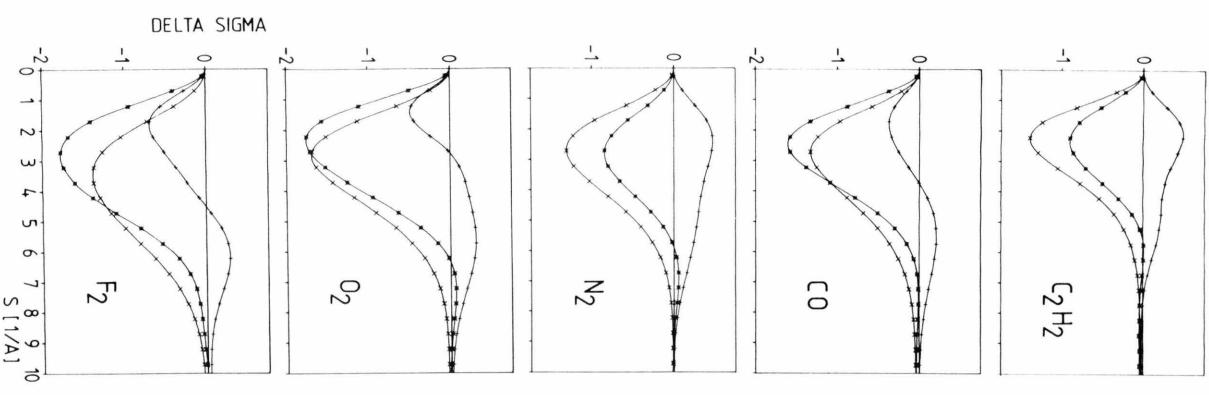


Fig. 3. Estimated full correlation corrections of the total (*), elastic (+) and inelastic (\times) $\Delta\sigma(s)$ curves.

ever, the position of the minimum is systematically shifted to higher values of s when passing from C_2H_2 to F_2 going parallel to the decreasing size of the constituent atoms. In particular, regarding future comparisons between theory and experiment it must be emphasized that taking electron correlation into account leads to inelastic scattering functions of comparable magnitude as the total scattering functions themselves.

Finally, the correlation corrected elastic scattering curves (not shown) resemble the AHF $\Delta\sigma_{\text{tot}}(s)$ curves in accordance with the finding that the corre-

lation corrected $\Delta\sigma_{\text{inelast}}(s)$ curves (Fig. 2) are similar to the correlation corrections of $\Delta\sigma_{\text{tot}}(s)$ (Figure 3).

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