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# Calculated scattering factor and diamagnetic susceptibility of $H_2S$

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# **Chimica fisica.** — *Calculated scattering factor and diamagnetic susceptibility of* $H_2S$. Nota di STEFANIN POLEZZO, MARIA PAOLA STABILINI e MASSIMO SIMONETTA, presentata [*] dal Corrisp. M. SIMONETTA.

RIASSUNTO. — Si presentano i calcoli del fattore di diffusione coerente dei raggi X e del contributo diamagnetico alla suscettività diamagnetica molare per la molecola $H_2S$, eseguiti impiegando una funzione d'onda SCF, e si fa il confronto dei risultati con i dati sperimentali.

In the present Note we employ the SCF wavefunction previously obtained [1] to calculate the $s$ and $p\sigma$ contributions to the X-ray coherent scattering factor $f$ [2] for a gas of $H_2S$ molecules. The value of $f$ is obtained through the formula

$$f^2(k) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} f_{lm}^*(k) f_{lm}(k) \tag{1}$$

where

$$f_{lm}(k) = (2\pi)^{3/2} \int_0^{\infty} \rho_{lm}(r) \frac{J_{l+1/2}(kr)}{(kr)^{1/2}} r^2 \, dr$$

$k = (4\pi \text{ sen } \theta/2)/\lambda$ ($\theta$ being the scattering angle and $\lambda$ the wavelength of the incident radiation), $\rho_{lm}(r)$ is the $l, m$ contribution to the electron density and $J_{l+1/2}(kr)$ are the Bessel functions of $l + 1/2$ order.

Of course, the main contribution is expected to come from the spherical electron density function, $\rho_{00}(r)$, due to the nearly spherical shape of the hydrogen sulphide molecule.

We outline here the method used to compute $\rho_{00}(r)$ and $\rho_{10}(r)$.

The total electronic density $\rho(r, \theta, \varphi)$ has been expanded in spherical harmonics about the sulphur nucleus

$$\rho(r, \theta, \varphi) = \sum_{p,q} P_{pq} \chi_p \chi_q^* = \sqrt{2} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \rho_{lm}(r) \, \Theta_l^m(\theta) \, e^{im\varphi}$$

where $P_{pq} = 2 \sum_i^{occ} c_{pi}^* c_{qi}$ are the density matrix elements computed from the coefficients reported in [1] and $\chi_p(r_p, \theta_p, \varphi_p)$ are the Slater type atomic orbitals on center $p$, choosen as basis ($1s_H$ on H and $1s$, $2s$, $2p$, $3s$, $3p$ and $3d$ on S). Therefore, in order to work out the $\rho_{00}$ and $\rho_{10}$ terms one has to expand about the sulphur atom the hydrogen orbitals

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[*] Nella seduta del 12 dicembre 1970.

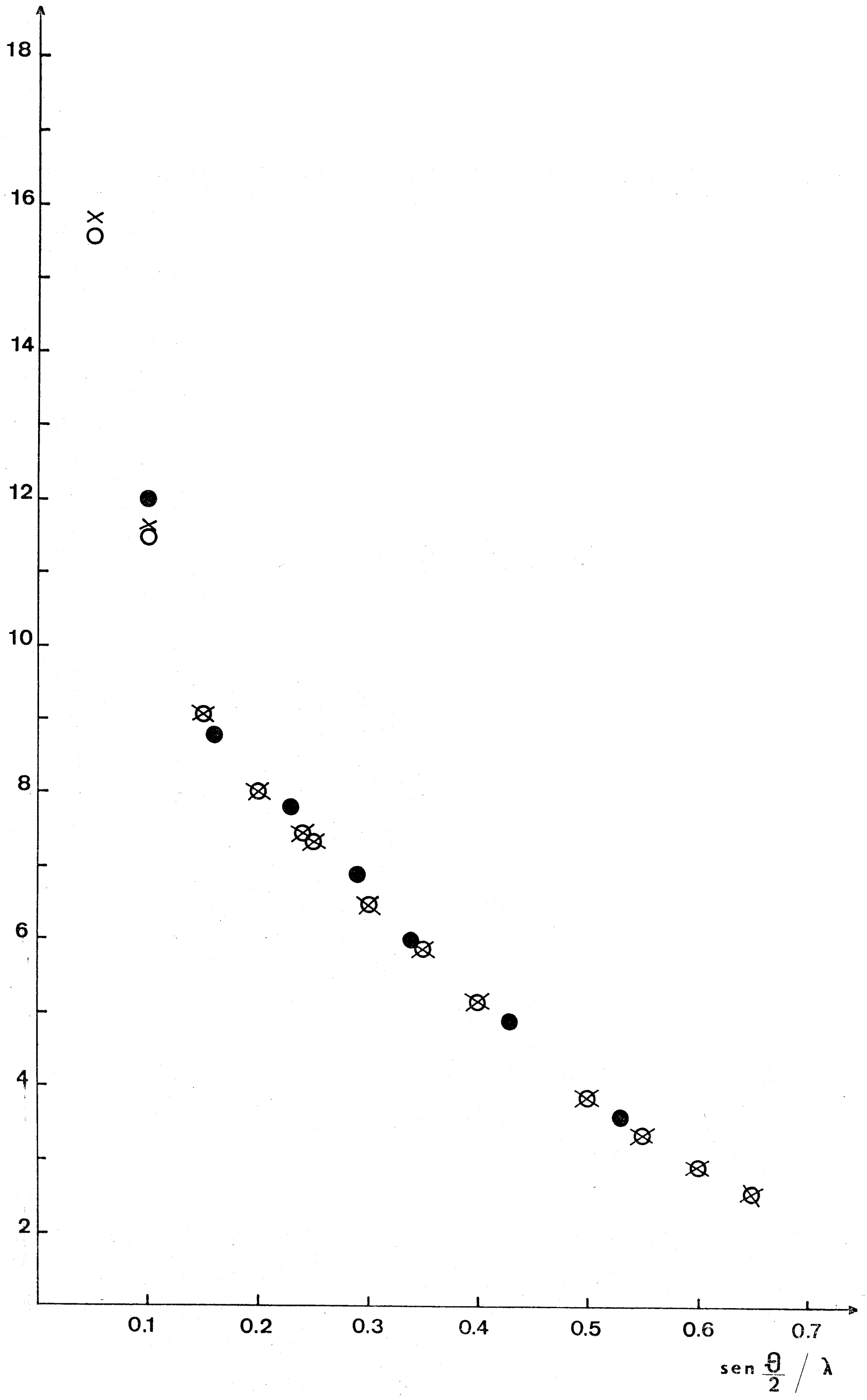

Fig. 1. – X–ray coherent scattering factor for $H_2S$ molecule;
○ $f_{00}(k)$ points; × $f(k)$ points; ● experimental points.

$h_{\pm} = (1\,s_{H_1} \pm 1\,s_{H_2})/\sqrt{2}$ and $|h_{\pm}|^2$. We employ the Barnett-Coulson expansion (see e.g. [3]) for $e^{-\beta r_{H_1}}$ and $e^{-\beta(r_{H_1}+r_{H_2})}$; and obtain;

$$h_{\pm} = \frac{2}{\sqrt{2}}\left(\frac{\beta}{\pi}\right)^{1/2} \sum_{\tau=0}^{\infty} \sum_{m=0}^{\tau}{}' \mathrm{D}_{\tau m}\, \mathrm{R}_{\tau}(r, \beta\,;\, \mathrm{R})\; \mathrm{P}_{\tau}^{m}(\alpha)\; \mathrm{P}_{\tau}^{m}(\vartheta) \cos m\varphi\,,$$

$$|h_{\pm}|^2 = \frac{\beta^3}{\pi}\left\{\sum_{\tau=0}^{\infty} \sum_{m=0}^{\tau}{}'' \mathrm{D}_{\tau m}\, \mathrm{R}_{\tau}(r, 2\beta\,;\, \mathrm{R})\; \mathrm{P}_{\tau}^{m}(\alpha)\; \mathrm{P}_{\tau}^{m}(\vartheta) \cos m\varphi \, + \right.$$

$$\pm \sum_{\tau,\tau'=0}^{\infty} \sum_{m,m'=0}^{\tau,\tau'} (-1)^{m'}\, \mathrm{D}_{\tau m}\, \mathrm{D}_{\tau' m'}\, \mathrm{R}_{\tau}(r, \beta\,;\, \mathrm{R})\; \mathrm{R}_{\tau'}(r, \beta\,;\, \mathrm{R}) \cdot$$

$$\left. \cdot\, \mathrm{P}_{\tau}^{m}(\alpha)\; \mathrm{P}_{\tau'}^{m'}(\alpha)\; \mathrm{P}_{\tau}^{m}(\vartheta)\; \mathrm{P}_{\tau'}^{m'}(\vartheta) \cos m\varphi\; \cos m'\varphi \right\}$$

where $\Sigma'$ means summing over $m$ even for $h_+$ and over $m$ odd for $h_-$ and $\Sigma''$ means summing over $m$ even,

$$\mathrm{D}_{\tau m} = (2 - \delta_{\tau 0})\,(l - |m|)!/(l + |m|)! \quad , \quad \mathrm{R}_{\tau}(r, \beta\,;\, \mathrm{R})$$

is expressed through Bessel functions as reported in [3] and $2\,\alpha$ is the $\widehat{\mathrm{HSH}}$ angle. Of course, only the first few terms of the first series are involved, as they must match with the corresponding angular part of the atomic orbitals on sulphur. On the other hand, the coefficients of $\mathrm{P}_0^0(\theta)$ and $\mathrm{P}_1^0(\theta)$ in the second series turn out to be quite rapidly convergent (less than 10 terms are sufficient).

In the fig. 1 the results of the calculation for $f_{00}(k)$ are plotted. The next contribution $f_{10}(k)$ to the scattering factor turns out to be appreciable only near the 0.1 point, so we can conclude that the inclusion of higher contributions surely would not make any significant addition and the use of only two terms in series (1) is justified. Therefore, the $f(k) = [f_{00}^2(k) + f_{10}^2(k)]^{1/2}$ curve is not sensibly different from the $f_{00}(k)$ curve as expected.

The experimental points, according to the values reported in the ref. [4], are also shown in the figure: as may be seen, the comparison is satisfactory.

We have also computed the purely diamagnetic contribution $\chi_d$ to the molar diamagnetic susceptibility [2] given by

$$\chi_d = -0.7923 \int_0^{\infty} r^2\, \rho_{00}(r)\, 4\pi r^2\, \mathrm{d}r = -33.9$$

which is in good agreement with the experimental value of $-32.7$.

After these calculations were completed a new ab initio calculation of the ground and excited states of $H_2S$ became available to us [5], in which more extended bases were used. However, the results for the ground state are pratically unchanged and do not warrant the use of these more complicated wavefunctions.

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