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LETTER TO THE EDITOR

Elastic scattering of electrons by HCN molecules in a two-potential hybrid approach at 21.6–700 eV

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Abstract. A previously employed two-potential coherent approach is used to investigate elastic scattering of electrons by HCN molecules at 21.6–700 eV. In this approach the short- and the long-range potentials (both spherical) are treated coherently and in addition the effects of multiple scattering within the molecule are also considered. The non-spherical part of the potential due to the permanent dipole moment of the molecule is treated in the first Born approximation (FBA) and added to the previous cross section (due to spherical potentials) incoherently. This hybrid two-potential method improves upon the well known independent-atom model (IAM) and is qualitatively superior to the FBA at intermediate energies (21.6 and 50 eV).

We have recently carried out extensive calculations on the elastic scattering of electrons by diatomic (Jain 1982) and linear polyatomic (Jain and Tayal 1982, Jain *et al* 1983) molecules at intermediate and high energies (40–1000 eV). For this purpose, we employed a two-potential coherent approach (Hayashi and Kuchitsu 1976a, b) in which the total interaction potential (isotropic part only) is divided into the short-range potential (centred at each atom of the molecule) and the long-range potential (centred at the centre of mass (COM) of the molecule) and the contributions to the cross section due to each potential are added coherently. In addition, the effects of multiple scattering within the molecule are also taken into account in this theory. This method has recently been explored for non-linear polyatomic molecules such as CCl_4 and As_4 by Daimon *et al* (1983*a*, *b*) who found that at intermediate energies the effects of intramolecular multiple scattering are significant enough to improve the independent-atom model (IAM) results. In this letter we repeat this theory for a linear polyatomic molecule with a permanent large dipole moment. It is well known that at very low energies ($\leqslant 10$ eV), the scattering mechanism for e–polar-molecule collisions is largely dominated by the nasty dipole interaction potential which is non-spherical and long range in nature. To deal with this dipole term, several approximate schemes have been proposed (see, for example, Norcross and Collins 1983); one salient feature of all these methods is the use of the first Born approximation. In fact, for large partial waves, the FBA becomes quite accurate. At somewhat higher energies ($E \geqslant 20$ eV), the dipole interaction is still influential, however other short-and long-range forces (spherical and non-spherical) become more and more important.

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It is, therefore, worth studying the e–polar-molecule (with a substantial dipole moment) scattering in the two-potential coherent approach with the dipole cross section calculated in the FBA and added incoherently to the cross section due to the spherical potentials (the short- and the long-range parts). The linear HCN molecule is a natural choice because of its large dipole moment ($D = 1.17$ au), its importance in the CN laser system and its presence in comets and interstellar medium. Almost no calculations exist for this system in the present energy regime. It is also interesting to note that HCN is isoelectronic with N_2, CO and C_2H_2 for which the present theory has been explored fully in this energy range (Jain 1982, Jain and Tayal 1982, Jain *et al* 1983); however, due to its different molecular expansion and large dipole moment (CO has a very small dipole moment which has an almost negligible effect at intermediate and high energies), the cross sections and polarisation effects are quite different. The present investigation is a first attempt to provide data on this system at intermediate and high electron energies. We use atomic units throughout this paper.

The details of the theory and the cross section formulae are given elsewhere (Hayashi and Kuchitsu 1976a, Jain 1982, Jain and Tayal 1982) and, therefore, we shall not repeat them here. In the present hybrid approach the final differential cross section is written as

$$\frac{d\sigma}{d\Omega} = \left(\frac{d\sigma}{d\Omega}\right)_{SPH} + \left(\frac{d\sigma}{d\Omega}\right)_{NSPH} \tag{1}$$

where the first differential cross section (DCS) term is due to the spherical (SPH) (short- and long-range parts) potential (see Jain and Tayal 1982), while the second non-spherical (NSPH) term arises due to the permanent dipole moment of the molecule. As mentioned earlier, we employ the FBA in order to evaluate $(d\sigma/d\Omega)_{NSPH}$, i.e. (Collins and Norcross 1978)

$$\left(\frac{d\sigma}{d\Omega}\right)_{NSPH} = \frac{2}{3}\frac{D^2}{k^2}\frac{1}{(1-\cos\theta)}. \tag{2}$$

Equation (2) is derived in the limit of the moment of inertia I of the molecule tending to ∞, k' (the final wavenumber of the outgoing electron) goes to k. In this limit, the momentum transfer is well defined by

$$\sigma_m^B = \frac{8\pi}{3k^2} D^2 \tag{3}$$

but the integral (σ_I^B) cross section is undefined. However, for a rotating dipole, let us take $I \neq \infty$ and $k' \neq k$, then (Collins and Norcross 1978)

$$\frac{d\sigma}{d\Omega}(J \to J';\theta) = \frac{4}{3} D^2 \frac{J_>}{2J+1}\frac{k'}{k}\frac{1}{k^2+k'^2-2kk'\cos\theta} \tag{4}$$

$$\sigma_M^B(J \to J') = \frac{8\pi}{3k^2} D^2 \frac{J_>}{2J+1}\left(1-\frac{(k-k')^2}{2kk'}\ln\frac{k+k'}{|k-k'|}\right) \tag{5}$$

and

$$\sigma_I^B(J \to J') = \frac{8\pi}{3k^2} D^2 \frac{J_>}{2J+1}\ln\frac{k+k'}{|k-k'|}. \tag{6}$$

Here $J' = J+1$, k'^2 is the kinetic energy of the outgoing electron and $J_>$ is the larger

of J and J'. All cross sections (equations (2)–(6)) are in the units of a_0^2 ($0.280\,03 \times 10^{-20}\,m^2$). If we sum on J', equations (4) and (5) reduce to equations (2) and (3), respectively, in the limit of I tending to ∞ and $k' = k$. On the other hand, equation (6) for the integral cross section becomes infinite. In our calculation, we use equation (6) to estimate σ_I^B and include only the $J = 10 \rightarrow J' = 11$ dipole excitation ($\Delta J = 1$), since at thermal temperature of the HCN molecules, the most probable ground state of the system is with $J = 10$.

In order to evaluate the first term of equation (1), we need several molecular parameters including those of polarisation potential such as the cut-off parameter and the dipole polarisability. Referring to the notations of our earlier paper (Jain and Tayal 1982), we have collected all such parameters for the e–HCN problem in table 1.

In the present calculations we have neglected exchange effects altogether. The contribution due to the non-spherical part of the polarisability α_2 ($\alpha_2 = 8.932$ au) is again calculated in the FBA and added incoherently in equation (2). A partial-wave analysis was performed to evaluate f_L and f_i. For f_i, the phaseshifts were included with high accuracy ($\sim 10^{-4}$) but the f_L phaseshifts could be calculated only up to an accuracy of 10^{-3} (for notations in this and the following paragraph see equations (1)–(9) of Jain and Tayal 1982).

Table 1. Molecular parameters for e–HCN elastic scattering.

Parameters	Value
R(HC)[a]	2.011 34 a_0
R(CN)[a]	2.185 26 a_0
R_H[b]	−2.955 24 a_0
R_C[b]	−1.020 94 a_0
R_N[b]	1.088 16 a_0
Dipole moment[c]	1.174 au
Dipole polarisability (α_0)[d]	17.50 au
Rotational constant[e]	1.478 22 cm^{-1} (1.833×10^{-4} eV)
Cut-off parameter (r_c)[f]	3.550 a_0

[a] R_{ij} of equation (4) of Jain and Tayal (1982).
[b] R_i of equation (1) of Jain and Tayal (1982).
[c] Bhattacharya and Gordy (1960).
[d] Landolt-Bornstein (1951).
[e] Herzberg (1966).
[f] Equation (9) of Jain and Tayal (1982), chosen arbitrarily.

In figure 1, we have shown the contributions of various multiple scattering terms ($I_{SD}^{(1)}$, $I_{SD}^{(2)}$ and $I_{DD}^{(0)}$) relative to I_S at 21.6 eV (curve A) and 50 eV (curve B). Summation over various l in equations (4)–(6) of Jain and Tayal (1982) converged well with about ten partial waves at these energies. The $I_{SD}^{(1)}$ (full curve A) term is the dominating (and negative throughout) term at both (and all) the energies. The $I_{DD}^{(0)}$ term is positive throughout and exhibits a peak around 90°. (This feature in the $I_{DD}^{(0)}$ term has also been found in N_2, CO, CO_2 and C_2H_2. In N_2 the peak is quite strong.) The contribution of the $I_{DD}^{(0)}$ decreases rapidly with an increase in energy; at 50 eV (broken curve) this term becomes very small and above this energy the contribution of this term is almost negligible. The $I_{SD}^{(2)}$ (chain curves) terms are oscillatory at both the energies, but very

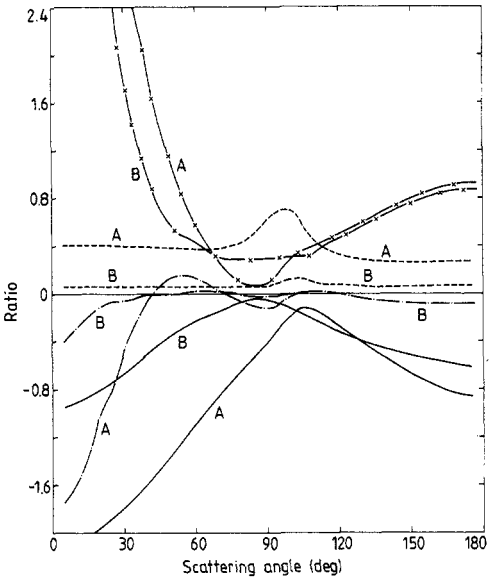

Figure 1. Multiple scattering terms (equations (4)–(7) with respect to I_S, equation (3) of Jain and Tayal 1982). Full curves, $I_{SD}^{(1)}$; broken curves, $I_{DD}^{(0)}$; chain curves, $I_{SD}^{(2)}$; with crosses I_{SS}. A is for 21.6 eV and B represents 50 eV curves.

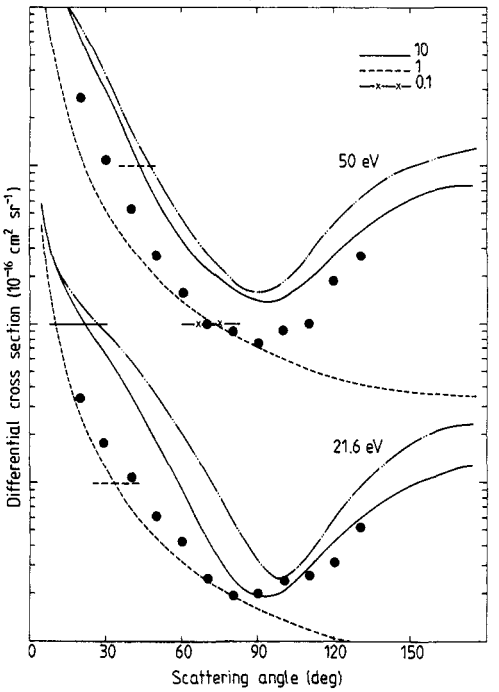

Figure 2. Elastic DCS for e-HCN scattering at 21.6 and 50 eV. Present calculations equation (1) full curve; present calculations without multiple-scattering terms, chain curves; the first Born approximation (FBA), using dipole term only, are shown by broken curves. The experimental data of Srivastava *et al* (1978) are plotted with full circles.

small at large angles. Also shown in this figure is the single scattering term (I_{SS}, curve with crosses) at both the energies.

Figure 2 displays our differential cross sections at 21.6 and 50 eV in three approximations: the full curves are the present full calculations (equation (1)); the chain curve is the result of equation (1) but without the multiple scattering terms and the broken curves are the FBA results using only the dipole term. It is quite clear from this figure that multiple scattering has a significant effect on the differential cross sections. All the three sets of results are compared with the absolute measurements of Srivastava *et al* (1978). The experimental error of these points is about ±18%. At 21.6 eV, the FBA seems to agree with experiment below 80°, but it does not reproduce a typical dip around 90°. (This dip is present in all other cases (N_2, CO, C_2H_2, CO_2) also below 100 eV.) It is also to be noted here that at very low energy the FBA gives fair results for e–polar-molecule scattering due to the strong dominance of dipole potential. The shape of the experimental data is faithfully reproduced in the present (full curves) cross sections at 50 eV, but the magnitude of this curve is larger by about a factor of two. The validity of the present model at 21.6 eV is doubtful.

There are no experimental data available above 50 eV energy. Our previous experience tells us that the present approach gives excellent results at and above 100 eV (Jain 1982, Jain and Tayal 1982, Jain *et al* 1983). In figures 3 and 4 we have

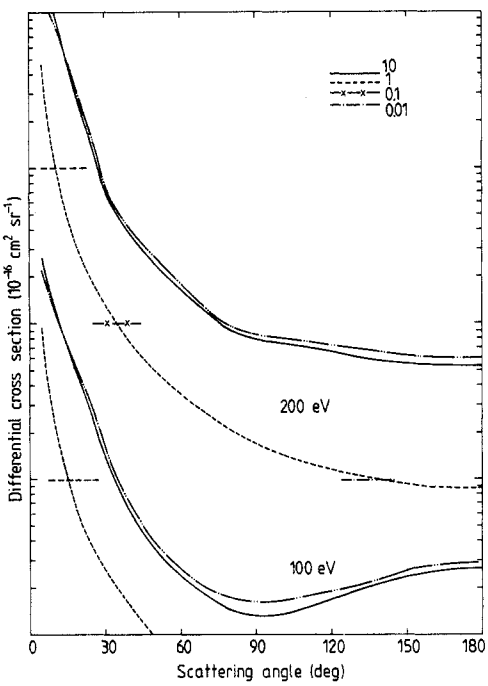

Figure 3. Same as figure 2, but for 100 and 200 eV.

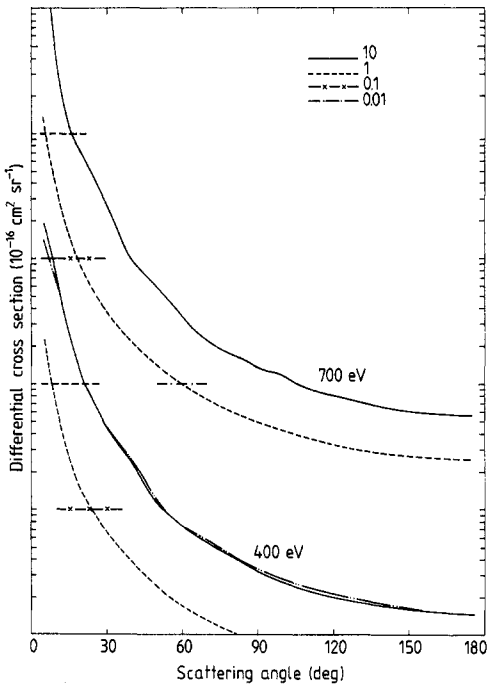

Figure 4. Same as figure 2, but for 400 and 700 eV.

shown our results at 100 and 200 eV and 400 and 700 eV, respectively. The Born results are too small at all energies. At 400 eV, the effect of multiple scattering terms is very small and at 700 eV it is hardly visible on the curves (not shown). It would be very interesting to have some experimental data at and above 50 eV to confirm the utility of the present model.

Since Srivastava *et al* (1978) have integrated their DCS to obtain integral (σ_I) and momentum transfer (σ_m) cross sections, we think it worthwhile to perform the same from our DCS. Unlike Srivastava *et al* who have integrated their DCS in various angular ranges, we have integrated our DCS only between 0 and 180°. The σ_m cross sections are given in table 2: there is very good agreement between theory and experiment at

Table 2. σ_m cross sections for e-HCN elastic scattering (in units of a_0^2).

Energy (eV)	Present equation (1)	FBA[a]	Experiment[b]
21.6	30.26	7.22	31.55 ± 6.43
50.0	17.18	3.12	23.21 ± 5.00
100.0	9.46	1.56	—
200.0	4.13	0.78	—
400.0	1.66	0.39	—
500.0	1.22	0.31	—
700.0	0.76	0.22	—

[a] Equation (3).
[b] Srivastava *et al* (1978).

both the energies where experimental data are available (the present results lie within the experimental error bars of Srivastava *et al*). However, it is worth noting that from the DCS curves of figure 2 at 21.6 and 50 eV, it appears that the present integrated cross section should be larger by about a factor of two than the experimental values of Srivastava *et al.* This discrepancy is certainly due to the extrapolated regions (see table III of Srivastava *et al*). In table 3, the present integral cross sections are compared with the approximate estimate of Srivastava *et al.* Our results again fall within the error bars except the result at 50 eV which is slightly below the lower bound of the experimental error bar. It is, however, to be noted that the FBA results σ_I^B in table 3 are not exact (we have not summed over J', equation (6), but included only one term corresponding to $J = 10$ and $J' = 11$). Despite this shortcoming in the FBA term, the results are encouraging. We do not claim that the present results are the best possible ones, however, keeping in mind the uncertainties also involved in the measured data, it is fair enough to say that the present hybrid approach is an initial satisfactory step towards more accurate calculations. The dipole potential is not effective at energies beyond about 500 eV. However, it dominates at the lower bound of the present energy region. In table 3, we have calculated the FBA results for σ_I only at 21.6 and 50 eV just for a direct comparison with experiment. At all other energies σ_I are calculated from equation (1) neglecting the second term. We have also repeated these calculations for e–SO_2 scattering and found encouraging results (Jain and Tayal 1983).

Table 3. σ_I cross sections for e-HCN elastic scattering (in units of a_0^2).

Energy (eV)	Present equation (1)	FBA[a]	Experiment[b]
21.6	127.16	72.50	124.99 ± 26.43
50.0	65.64	33.96	99.99 ± 21.67
100.0	22.57[c]	—	—
200.0	14.84[c]	—	—
400.0	9.06[c]	—	—
500.0	7.54[c]	—	—
700.0	5.63[c]	—	—

[a] Equation (6).
[b] Srivastava *et al* (1978).
[c] Equation (2) (without dipole term).

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