A new ionospheric scattering mechanism

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(Received in final form 25 June 1982)

Abstract—The attachment of free electrons to neutral molecules followed by detachment from the resulting negative ions leads to fluctuations of the electron density in the lower ionosphere. Such fluctuations, superimposed on thermal fluctuations, enhance the scattering cross-section for an incident electromagnetic wave. A simple analytical expression of the cross-section is demonstrated independently by a thermodynamical method and by a stochastic formulation. Furthermore, a numerical simulation of the fluctuating electron concentration leads to a numerical cross-section profile which agrees with the theoretical expression.

1. INTRODUCTION

The propagation of an electromagnetic wave in the terrestrial atmosphere can be used not only as a communication tool, but also as a detection technique which provides physical information on the interacting medium. Three mechanisms essentially may affect any propagating wave, i.e. absorption, reflection and scattering. The initial idea (GORDON, 1958) that a large antenna would make it possible to detect the Thomson scattering of radar signals from the ionosphere led to considerable developments of incoherent scattering stations (see BEYNON and WILLIAMS, 1978). Until very recently this technique produced fundamental geophysical results for the atmospheric regions above 100 km altitude (Evans, 1969; Alcaydé 1979; Alcaydé and Bernard, 1982), but technological developments in large VHF and UHF radars have led to a systematic analysis (WALKER, 1979; HARPER and GORDON, 1980) of scattered signals either by the ionosphere or by the neutral atmosphere from ground level up to high altitudes.

Scattering in a random continuum is always a consequence of some fluctuations of the ambient dielectric constant (ISHIMARU, 1978) which enters into Maxwell's equations for the propagation of electromagnetic waves. Such fluctuations may result from water vapour fluctuations in the lower troposphere, from vertical gradients in the refractive index, from turbulence and from electron density fluctuations (VILLARS and WEISSKOPF, 1955; GALLET, 1955; HARPER and GORDON, 1980). The physical origin of a scattered ionospheric signal is usually attributed to thermal fluctuations of the ambient electron density. Various theoretical approaches of the scattered signal have been described (see BAUER, 1975) by taking into account electron—ion collisions, electron—neutral collisions and

magnetic field effects. More recently, the effect of negative ions, present below 100 km altitude, has been considered (MATHEWS, 1978; FUKUYAMA and KOFMAN, 1980) as an important factor enhancing the Thomson scattering cross-section in a collision-dominated medium. We have modified this theory (KOCKARTS and WISEMBERG, 1981) in order to account for electron fluctuations resulting from chemical reactions. Such fluctuations produce a further enhancement of the scattering cross-section in the terrestrial D-region over the height range where negative ions become comparable with, or greater than, the ambient electron concentration. The matrix formalism we used for such an extension does not perhaps provide enough physical insight into the mechanism. Such a formalism, however, was used to recover simultaneously the results of MATHEWS (1978) and FUKUYAMA and KOFMAN (1980) while introducing the effect of chemical fluctuations. This paper, therefore, is intended to clarify the effect of chemical fluctuations by isolating the physical phenomenon.

A classical thermodynamic approach will lead to the same result as a stochastical point of view and the theoretical expression for the contribution of chemical fluctuations to the incoherent scattering cross-section will be confirmed by a numerical simulation using computed electron density fluctuations.

2. CHEMICAL FLUCTUATIONS

When free electrons are produced in the *D*-region below 80 km by external ionizing agents such as solar Lyman- α radiation, X-rays and particle precipitations, a complex set of chemical reactions (Ferguson *et al.*, 1979; SMITH and ADAMS, 1980) leads to a production of negative ions which can be lost to some extent by

recombination with positive ions, by collisional detachment and by photodestruction. A detailed composition model requires the introduction of more than 100 chemical reactions involving charged and neutral particles. Using signal-flow graph theory, we have shown (WISEMBERG and KOCKARTS, 1980: KOCKARTS and WISEMBERG, 1981) the possibility of constructing an equivalent model whose phenomenological characteristics are given in Fig. 1. The mean recombination coefficients α_e and α_- are easily determined from a detailed composition model. The electron loss rate L_{e} and the negative ion loss rate L_{-} are rigorously computed with the signal-flow graph theory. Results are presented in Fig. 2 which also shows the electron loss rate $\alpha_e n_+$ by recombination with positive ions. In the region where negative ions become important (<80 km) $\alpha_e n_+$ is always negligible compared to L_e . The loss rate $\alpha_- n_+$ is so low that it cannot be represented in Fig. 2. As a consequence of the processes converting electrons into negative ions and vice versa, it is conceivable that a fluctuation of the electron concentration occurs around an equilibrium value since the characteristic times L_e^{-1} and L_e^{-1} are finite quantities different from zero. Considering only the processes represented by the full lines in Fig. 1, the equilibrium concentrations \bar{n}_e and \bar{n}_- for the electron and negative ions are related by $\bar{n}_e L_e = \bar{n}_- L_-$ in the height range where negative ions play a significant role. If we assume that the instantaneous electron and negative ion concentrations n_e and n_{-} fluctuate around their respective equilibrium values such that $n_e = \bar{n}_e + n'_e$ and $n_{-} = \bar{n}_{-} + n'_{-}$, the fluctuating quantities n'_{-} and n'_{-} always have opposite signs since the total number of particles $n_e + n_-$ is invariant. As a result of the continuity equation, the time-derivative of the fluctuating part n'_{e} , in the absence of any bulk motion, is then given by

$$\frac{\mathrm{d}n_{\mathrm{e}}'}{\mathrm{d}t} = -(L_{\mathrm{e}} + L_{-})n_{\mathrm{e}}'. \tag{1}$$

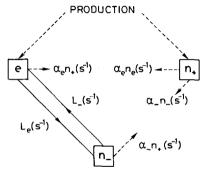


Fig. 1. Schematic representation of the physical process involved in an equivalent model of the *D*-region.

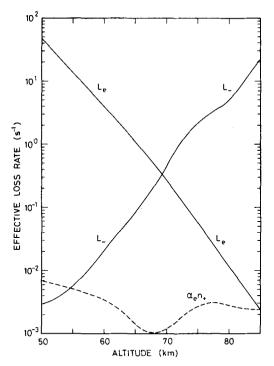


Fig. 2. Vertical profiles of the effective loss rates for electrons (L_e) and negative ions (L_-) in an equivalent model. The dashed curve gives the electron loss rate by neutralization with positive ions.

Below 80 km altitude, the contributions of electron—ion recombination and ion—ion recombination to the fluctuations n'_{e} and n'_{-} are negligible since $\alpha_{-}n_{+}$ and $\alpha_{e}n_{+}$ are always much smaller than L_{e} or L_{-} (see Fig. 2).

Equation (1) is a scalar form of a phenomenological matrix equation analysed in great detail by DE GROOT and MAZUR (1962) in the statistical theory of thermodynamics. When a random or stochastic force term is added to the right-hand member, it becomes a Langevin equation of the same type as that used to describe Brownian motion. The present fluctuation is, however, of chemical origin and it is superimposed on the thermal fluctuation of the electrons. This means that any theory of incoherent scattering based on purely electron thermal fluctuations ignores any possible effect of the reversible conversion of electrons into negative ions.

3. SCATTERING CROSS-SECTION

The average differential scattering cross-section for backscattering of an incident electromagnetic wave with angular frequency ω_0 is given by DOUGHERTY and FARLEY (1960) as

$$\sigma(\omega_0 \pm \omega) d\omega = r_e^2 V \langle n_e^{\prime 2}(\omega) \rangle d\omega, \qquad (2)$$

where $\langle n_e^2(\omega) \rangle = S(\omega)$ is the frequency power spectrum of the fluctuation occurring in a volume V and r_e is the classical electron radius. According to the Wiener-Khinchin theorem (see DE Groot and Mazur, 1962), the power spectrum of a stationary process is the Fourier transform of the autocorrelation function of the fluctuating part. This autocorrelation function $\varphi(t)$ is easily deduced by integration of equation (1) and it can be written as

$$\varphi(t) = \langle n_e^{\prime 2} \rangle \exp \left[-(L_e + L_-)|t| \right], \tag{3}$$

where $\langle n_e^2 \rangle$ is the mean square of the fluctuating part at equilibrium t = 0. The frequency power spectrum is then given by

$$S(\omega) = \frac{1}{\pi} \langle n_{\rm e}^{\prime 2} \rangle \frac{(L_{\rm e} + L_{-})}{\omega^2 + (L_{\rm e} + L_{-})^2} = \langle n_{\rm e}^{\prime 2}(\omega) \rangle, \quad (4)$$

where we have to evaluate the mean square $\langle n_e^2 \rangle$ of the fluctuations at equilibrium in order to obtain an analytical expression for the scattering cross-section.

3.1. Thermodynamical approach

In a system where entropy modifications are induced only by chemical reactions, the mean square of the fluctuations is related to affinities of the reactions (PRIGOGINE, 1968). The affinity A for the reaction converting electrons into negative ions is

$$A = kT \ln \left[(N_e L_e)/(N_- L_-) \right], \tag{5}$$

where $N_{\rm e}$ and N_{-} are the number of electrons and negative ions, k is Boltzmann's constant and T is the temperature. When $N_{\rm e}=\bar{N}_{\rm e}+N'_{\rm e}$ and $N_{-}=\bar{N}_{-}+N'_{-}$, the affinity at equilibrium is zero $(\bar{N}_{\rm e}L_{\rm e}=\bar{N}_{-}L_{-})$ and equation (5) can be transformed as

$$A = kT(N'_{e}/\bar{N}_{e})(L_{e} + L_{-})/L_{e}, \tag{6}$$

expressing that the fluctuation of the affinity is directly proportional to the fluctuation $N'_{\rm e}$ of the number of electrons. The mean square of the fluctuations (PRIGOGINE, 1968) around the equilibrium value $\bar{N}_{\rm e}$ is then given by

$$\langle N_e^{\prime 2} \rangle = kT(\partial A/\partial N_e^{\prime})^{-1} = \bar{N}_e L_e/(L_e + L_-), \quad (7a)$$

or

$$\langle n_e^{\prime 2} \rangle = \bar{n}_e V^{-1} L_e / (L_e + L_-),$$
 (7b)

since

$$N_e = n_e V$$
.

This result can also be obtained as a direct consequence of the fluctuation-dissipation theorem (see DE GROOT and MAZUR, 1962; PRIGOGINE, 1968) by considering the fluctuation N'_e as a flux and the affinity

A as its thermodynamical conjugated force in equation (6).

Expressions (7) can be compared with the mean square of the fluctuations in an ordinary ideal gas which is simply equal to the average number of particles (LIFSHITZ and PITAEVSKII, 1980). Noting that $\langle N'_e \rangle = \langle n'_e \rangle V$, we obtain with equations (2), (4) and (7) the following expression for the scattering cross-section

$$\sigma(\omega_0 \pm \omega) d\omega = \frac{r_e^2}{\pi} \left[\frac{\bar{n}_e L_e}{\omega^2 + (L_e + L_-)^2} \right] d\omega. \quad (8)$$

3.2. Stochastical approach

Another elegant way to study the effect of chemical fluctuations is to use a stochastical approach for chemical kinetics (McQuarrie, 1967; Nicolis and PRIGOGINE, 1977). Only a few elementary reactions are exactly solvable. This is the case for the reversible process $n_a \rightleftharpoons n_-$ for which the solution of the master equation gives simultaneously the time evolutions of the average number of particles and its variance. A time-dependent analytical expression of the variance $\langle (N_c - \bar{N}_c)^2 \rangle = \langle N_c^2(t) \rangle$ leads immediately to an expression for the fluctuation around the equilibrium $(t \to \infty)$. Fluctuations are recognized through the second central moment, or variance. When the stochastic expression (McQuarrie, 1963) for the variance of a reversible first-order reaction is applied at equilibrium, we find immediately equation (7a) without introducing the affinity. As a consequence, the validity of expression (8) for the scattering crosssection is thus demonstrated by another independent approach.

3.3. Ionospheric importance

A measurement of the half-width of the scattering cross-section gives $L_e + L_-$ and the zero frequency shift value leads to $L_e/(L_e+L_-)$ if the equilibrium value \tilde{n}_e is known. We see that the ratio $\lambda = L_e/L_-$ between the abundances of negative ions and electrons can be obtained from such measurements. In our matrix formulation (KOCKARTS and WISEMBERG, 1981) we presented expression (8) without demonstration, since the objective was to obtain a general formulation taking into account chemical and thermal fluctuations. The Lorentzian peak given by expression (8) is actually superimposed on the cross-sections solely based on thermal fluctuations. When L_e becomes small, L₋ automatically becomes large and the contribution of chemical fluctuations disappears, since the reversible process $n_{e} \rightleftharpoons n_{-}$ does not affect anymore the fluctuation of the electron concentration. This happens in the terrestrial D-region for altitudes above 80 km. In the lowest part of the D-region where the electron concentration is negligible, the effect will be undetectable because of the weakness of the backscattered power. The exact height interval at which the phenomenon should be observable depends on the variable ionospheric structure. Values of L₂ and L_{-} given in Fig. 2 are only indicative for geophysically quiet conditions and incoherent scattering measurements in the D-region should give their exact values as well as their dependence on geophysical parameters. When experimental values for L_a and L_{\perp} are available. they could be used in reverse with a signal-flow graph model (WISEMBERG and KOCKARTS, 1980) to see the relative importance of the chemical processes responsible for the presence of negative ions in the Dregion.

The relative importance of the contribution of chemical fluctuations to the total scattering cross-section has been shown by Kockarts and Wisemberg (1981). In order to emphasize again the phenomenon, we have compared in Fig. 3 the ratios of the ionic power to the total power P_{tot} of incoherent scatter spectra when the ionic power (curves P_i/P_{tot}) is computed from the theory of Mathews (1978) and Fukuyama and Kofman (1980) or when the ionic power (curves P_{i+c}/P_{tot}) includes the effect of chemical fluctuation. Below 70 km altitude the difference between the two ratios becomes very large and it should be observable. Since the chemical fluctuations are purely temporal no dependence of the transmitter wavelength appears in expression (8). This is not the case for the whole

incoherent scatter spectrum and, as a consequence, the full curves in Fig. 8 correspond to a radar frequency of 935 MHz (Saint-Santin) and the dashed curves are for 430 MHz (Arecibo). We see that the contribution of chemical fluctuations extends to greater heights for higher radar frequencies.

4. NUMERICAL SIMULATION

The deterministic formulation without transport of a mixture of reacting species is based on a set of coupled ordinary differential equations in which the reaction constants are viewed as reaction 'rates' and the concentrations are continuous functions of time. The stochastic formulation considers the reaction constants as reaction probabilities per unit time and the concentrations are actually integer numbers involved in a master equation giving the probability of finding various populations as a function of time. It has been stressed several times (McOuarrie, 1967; Gillespie, 1977) that the stochastic formulation of chemical kinetics has a firmer physical basis than the deterministic formulation, even if the master equation is often mathematically intractable. An exact numerical method, however, has been developed by GILLESPIE (1976) to simulate the stochastic formulation of any spatially homogeneous mixture of reacting species. Numerical applications (GILLESPIE, 1977) for nonlinear systems near chemical instabilities have demonstrated the utility of the simulation algorithm.

The theory of GILLESPIE (1976) for a system of μ

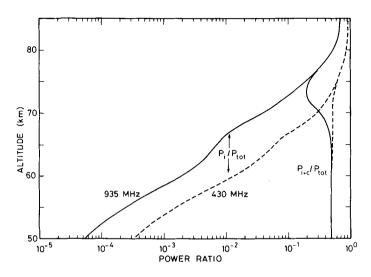


Fig. 3. Height distribution of the ratio between ionic power and total power. Curves P_i/P_{tot} neglect the contribution of chemical fluctuations whereas P_{i+c} includes the contribution of the cross-section (8) integrated over frequency. Full curves are for a radar frequency of 935 MHz and dashed curves correspond to 430 MHz.

reactions is based on the computation of a reaction probability density function given by

$$P(\tau, \mu) = P_1(\tau)P_2(\tau, \mu), \tag{9}$$

where $P_1(\tau) d\tau$ is the probability at time t that the next reaction in a volume V will occur in the differential time interval $(t+\tau, t+\tau+d\tau)$ and $P_2(\tau, \mu)$ is the probability that it will be reaction μ . In our simple reversible process $n_e \rightleftharpoons n_-$, Gillespie's theory leads to

$$P_{1}(\tau) = (N_{e}L_{e} + N_{-}L_{-}) \exp \left[-(N_{e}L_{e} + N_{-}L_{-})\tau\right], \tag{10}$$

and

$$P_2(\tau, \mu) = \frac{N_{\mu}L_{\mu}}{N_{c}L_{c} + N_{-}L_{-}},\tag{11}$$

where μ is either index e or index — and $N_{\rm e}$ and $N_{\rm L}$ are the numbers of electrons and negative ions. The time τ is obtained from

$$\tau = (N_{c}L_{c} + N_{-}L_{-})^{-1} \ln r_{1}^{-1}, \tag{12}$$

where r_1 is a random number between 0 and 1. The reaction occurring (electron loss or negative ion loss) is determined by the index μ which leads to the inequality

$$N_{\mu}L_{\mu} \geqslant r_2(N_eL_e + N_-L_-),$$
 (13)

where r_2 is another random number between 0 and 1. It is then easy to update N_e and N_- by adding one to N_e and subtracting one from N_- or by subtracting one from N_e and adding one to N_- depending on which reaction satisfies condition (13).

We have applied Gillespie's method to the analysis of the fluctuations of the simple reversible process $n_a \rightleftharpoons n_$ around its equilibrium. As an example, the fluctuation $N_c - \bar{N}_c$ around the equilibrium value \bar{N}_c is shown in the upper part of Fig. 4 which corresponds to an altitude of 60 km in our equivalent ionospheric model. Starting with six electrons, we sample 100 values at 5×10^{-2} s intervals over a total time of 5 s. The average time interval between two reactions is $1/(\bar{N}_e L_e + \bar{N}_- L_-)$. At 60 km, this time is 2.1×10^{-2} s, so that 260 changes of N_e occurred during the 5 s shown in Fig. 4. Although Gillespie's method accounts for each single reaction occurring in the system, it is a simple matter of programming to obtain snapshots of the fluctuating system at constant time intervals. It is also remarkable that the variance of the 100 points in Fig. 4 is 5.93 whereas the theoretical variance $\bar{N}_e L_e / (L_e + L_-)$ from McQuarrie (1963) is 5.97. This can be considered as a confidence test for the sampling rate adopted in Fig. 4. Considering the sampled points as data points it is now possible to estimate the power spectrum resulting from these fluctuations.

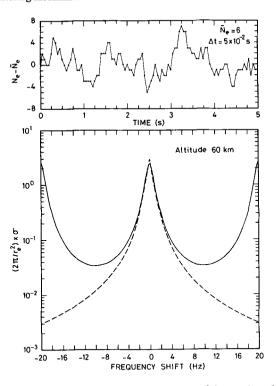


Fig. 4. The upper part gives the fluctuations of the number of electrons around the mean value \bar{N}_e at 5×10^{-2} s time intervals over a period of 5 s. The full curve in the lower part is the corresponding power spectrum as a function of frequency shift. The dashed curve corresponds to the theoretical expression (8).

The classical method which consists in computing the Fourier transform of the autocorrelation function, has been tried without success, probably as a consequence of an insufficient number of points. This is easily understood in Fig. 5 which shows a comparison between the theoretical autocorrelation function given by expression (3) and the numerical values computed with the points given in the upper part of Fig. 4. We have, therefore, used the maximum entropy method (MEM) whose historical development and practical applications are described in a volume of the IEEE selected reprint series (CHILDERS, 1978). The name of the method arises from a mathematical similarity between an expression for the entropy in thermodynamics and a statistical evaluation of the information as a function of the probability of occurrence for a particular state (Brillouin, 1956). Entropy is, however, not a measure of disorder in a system nor a measure of our ignorance about the actual structure (TONNELAT, 1978). The name of the method is, therefore, misleading and we prefer to adopt a name such as maximum

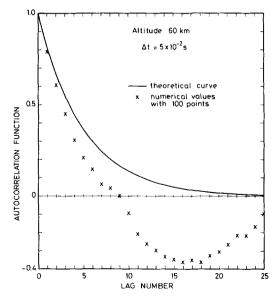


Fig. 5. Autocorrelation function computed with expression (3) at 60 km altitude (full curve). Crosses represent the autocorrelation obtained with the fluctuations shown in Fig. 4.

information method (MIM). We have adapted a Fortran program (ULRYCH and BISHOP, 1975) in APL and we used AKAIKE's (1969) criterion to determine the best autoregressive order for the fluctuating process. For the present chemical fluctuations, numerical applications of this criterion lead always to first order autoregressive processes. The full curve of the lower part of Fig. 4 gives the power spectrum obtained by MIM from the fluctuations shown in the upper part. The dashed curve results from the theoretical expression (8). The agreement between theory and simulation is excellent over a range of frequency shifts of ± 5 Hz. The simulated spectrum shows a periodic structure beyond 10 Hz as a logical consequence of the sampling frequency (20 Hz) which according to Shannon's theorem (see Max, 1980) forbids a correct representation of the power spectrum beyond 10 Hz. A remedy to this situation is easily obtained by increasing the sampling frequency. Nevertheless, Fig. 4 clearly indicates that GILLESPIE's (1976) simulation method can lead to a power spectrum in agreement with our theoretical expression.

The simulation becomes more difficult when the power spectrum is very narrow, as is the case for example at 70 km where $L_e = 0.271 \text{ s}^{-1}$ and $L_- = 0.777 \text{ s}^{-1}$. A simulated spectrum obtained with 1000 points sampled at 5×10^{-3} s time intervals is shown in the lower part of Fig. 6. The deviation from the theoretical spectrum is given in the upper part and again the agreement can be considered as excellent

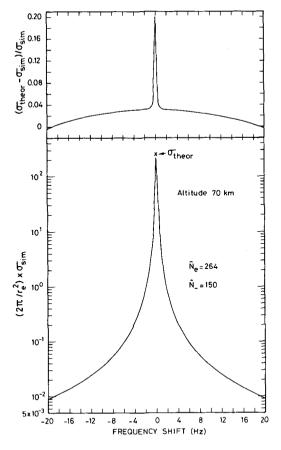


Fig. 6. The lower part gives the simulated scattering cross-section $\sigma_{\rm sim}$ by the maximum information method with 1000 points at 5×10^{-3} s time intervals around a mean number of electrons $\bar{N}_{\rm e}$. The upper part shows the deviation from the theoretical value $\sigma_{\rm theor}$.

over ± 20 Hz frequency shift. The periodicity of the simulated spectrum does not appear in Fig. 6 since the sampling frequency is 200 Hz. The variance of the fluctuations is 86 which is comparable to the value 96 for theoretical variance. Numerous simulations have been made for other altitudes and it has always been possible to match the simulated spectrum with the theoretical spectrum by adjusting either the sampling frequency or the total sampling time or both. The best agreement at zero frequency shift is always obtained when the sampled fluctuations lead to a variance comparable with the theoretical variance $\bar{N}_c L_c / (L_c + L_-)$.

In conclusion we have shown that the theoretical expression (8), obtained by two different approaches, can be simulated numerically by an independent method. Such a new ionospheric scattering mechanism has to receive its experimental confirmation. If the technical feasability of systematic observations could

be proven with large radar systems, chemical fluctuations of the *D*-region electron concentration could provide an excellent tool to measure the ratio $\lambda=\bar{n}_-/\bar{n}_{\rm e}=L_{\rm e}/L_-$ between negative ions and electrons.

Acknowledgements—We thank G. NICOLIS and J. DE PRINS (Université Libre de Bruxelles) for helpful advice on thermodynamic fluctuations and power spectrum analysis and F. Bertin and A. Crémieu (Centre de Recherches en Physique de l'Environnement terrestre et planétaire, Paris) for numerous discussions on ionospheric incoherent scattering.

REFERENCES

REFERENCES		
Akaike H.	1969	Ann. Inst. statist. Math. 21, 243.
Alcaydé D.	1979	Space Res. 19, 211.
ALCAYDÉ D. and BERNARD R.	1982	J. atmos. terr. Phys. 44, 95.
BAUER P.	1975	Phil. Trans. R. Soc. London A280, 167.
BEYNON W. J. G. and WILLIAMS P. J. S.	1978	Rep. Prog. Phys. 41, 909.
Brillouin L.	1956	Science and Information Theory, p. 159. Academic Press, New York.
CHILDERS D. G. (Editor)	1978	Modern Spectrum Analysis. IEEE Press, New York.
DE GROOT S. R. and MAZUR P.	1962	Non-equilibrium Thermodynamics. North-Holland, Amsterdam.
DOUGHERTY J. P. and FARLEY D. T.	1960	Proc. R. Soc. London A259, 79.
Evans J. V.	1969	Proc. IEEE 57, 496.
FERGUSON E. E., FEHSENFELD F. C. and ALBRITTON D. L.	1979	Gas Phase Ion Chemistry (Edited by M. T. Bowers) Academic Press, New York.
FUKUYAMA K. and KOFMAN W.	1980	J. Geomag. Geoelect. 32, 67.
GALLET R. M.	1955	Proc. IRE 43, 1240.
GILLESPIE D. T.	1976	J. comp. Phys. 22, 403.
GILLESPIE D. T.	1977	J. phys. Chem. 81 , 2340.
GORDON W. E.	1958	Proc. IRE 46, 1824.
HARPER R. M. and GORDON W. E.	1980	Radio Sci. 15, 195.
Ishimaru A.	1978	Wave Propagation and Scattering in Random Media, Vol. 2. Academic Press, New York.
Kockarts G. and Wisemberg J.	1981	J. geophys Res. 86, 5793.
LIFSHITZ E. M. and PITAEVSKII L. P.	1980	Statistical Physics Part 1. Pergamon Press, Oxford.
Mathews J. D.	1978	J. geophys. Res. 83, 505.
Max J.	1980	Méthodes et Techniques de Traitement du Signal. Masson, Paris.
McQuarrie D. A.	1963	J. chem. Phys. 38, 433.
McQuarrie D. A.	1967	Stochastic Approach to Chemical Kinetics. Methuen, London.
NICOLIS G. and PRIGOGINE I.	1977	Self-Organization in Non-equilibrium Systems. Wiley, New York.
PRIGOGINE I.	1968	Introduction à la Thermodynamique des Processus Irréversibles. Dunod, Paris.
SMITH D. and ADAMS N. G.	1980	Topics in Current Chemistry, Vol. 89. Springer, Berlin.
Tonnelat J.	1978	Thermodynamique et Biologie, Vol. 1, p. 202. Maloine- Doin, Paris.
ULRYCH T. J. and BISHOP T. N.	1975	Rev. Geophys. Space Phys. 13, 183.
VILLARS F. and WEISSKOPF V. P.	1955	Proc. IRE 43, 1232.
Walker J. G. C.	1979	Science 206 , 180.
WISEMBERG J. and KOCKARTS G.	1980	J. geophys. Res. 85 , 4642.