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Environmental applications of electron–molecule interactions

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ABSTRACT

The significance of basic knowledge on low-energy electron–molecule interactions to environmental and energy issues is illustrated by three examples: electric power transmission and distribution, destruction of toxic chemicals in the environment, and new materials for renewable energy sources.

1. Introduction

While the role of low-energy electron–molecule interactions in efforts to solve environmental problems and develop new energy technologies and materials has long been documented (e.g., see [1–5] and references cited therein), much is still needed to bring the field of low-energy electron–molecule interactions closer to the environmental problems and the energy issues. For instance, knowledge on electron–molecule interactions can help provide alternative materials which are environmentally more friendly than those in current use. It can also help elucidate the role of electron-interaction processes in the environment *vis-a-vis* photon interactions and in the development of new materials for energy uses.

In this paper we discuss the use of knowledge on electron–molecule collisions to (1) develop environmentally friendly gaseous media for electric power transmission and distribution, (2) destroy environmental pollutants by low-energy electrons, and (3) tailor new materials for renewable energy sources.

2. Development of N_2/SF_6 mixtures for electric power transmission and distribution

Basic and applied research in gaseous dielectrics and engineering tests on prototypical gas-insulated equipment over the last few decades (e.g., see [6–13] and sources cited therein) have generated fundamental knowledge which allowed the identification and tailoring of gaseous insulators for use by the electric power industry in the transmission and distribution of electric energy. Gaseous dielectrics are presently used in circuit breakers (CBs), substations (GISs), transmission lines (GILs), transformers (GITs), and other high-voltage equipment, such as particle accelerators and gas lasers. Gas-insulated equipment is now a mature technology: it is compact, easy to repair, conserves energy, protects the environment, avoids possible health effects, and works well.

In these applications, the insulating gas must be environmentally acceptable at all times. However, the gas most commonly used to date by the electric power industry as an insulting and switching medium, namely sulfur hexafluoride SF_6, has been found to be a potent greenhouse gas [12,14]. It is an efficient absorber of infrared radiation, particularly near 10.5 μm and it is largely immune to chemical and photolytic decomposition. Hence, the lifetime of SF_6 in the environment is very long (half time ~3200 years) and its global warming potential extremely high (~25,000 times higher than that of CO_2) [14]. Thus, while the concentration of SF_6 in the environment is presently low [12] its contribution to global warming is expected to be cumulative and virtually permanent. SF_6 is one of the six greenhouse gases on the Kyoto Protocol List, drafted ~20 years ago.

Basic knowledge on electron–molecule interactions has led to at least a partial solution to this problem. The basic physics of gaseous dielectrics has shown that of the multitude of processes that take place in an electrically stressed gas, the most significant are those that involve free slow electrons and their interactions with the molecules of the insulating gas (e.g., see [6–9]). Foremost among

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Table 1
Basic physics of gaseous dielectrics

For a non-electronegative (non-electron attaching) gas such as N_2
$(E/N)_{\mathrm{lim}}$ is small, determined by $\alpha/N \rightarrow 0$

For an electronegative (strongly electron attaching) gas such as SF_6
$(E/N)_{\mathrm{lim}}$ is large, determined by $\alpha/N = \eta/N$

The dielectric strength of a gaseous insulator can be optimized by using basic knowledge on electron–gas molecule collisions
Ionization coefficient α/N (E/N) must be small
Electron attachment coefficient $\eta/N(E/N)$ must be large
Electron energy distribution $f(\varepsilon, E/N)$ must be shifted to lower energies to minimize electron production and maximize electron removal by attachment

these interactions are the processes which control the number densities and electron energies in the electrically stressed dielectric: those which generate electrons via ionization, those which deplete electrons via electron attachment, and those which control the electron energies via electron scattering from molecules. Actually, so important is the ability of a gas dielectric to remove electrons via electron attachment in determining its dielectric strength that gaseous dielectric media have been separated into those which attach electrons, called electronegative, and those which do not attach electrons, called non-electronegative. The dielectric strength of the former is high and that of the latter is low [6–9].

If $\alpha/N(E/N)$, $\eta/N(E/N)$, and $f(\varepsilon,E/N)$ are, respectively, the electron-impact ionization coefficient, the electron attachment coefficient and the electron energy distribution function as a function of the density-reduced uniform electric field E/N, the limiting value, $(E/N)_{\mathrm{lim}}$, of E/N (that is, the value of E/N at which breakdown occurs), is determined as shown in Table 1.

The basic knowledge on electron-impact ionization, electron attachment and electron slowing down via scattering led to the concept of the multicomponent gaseous insulator [6,7], where electron scattering and electron attaching gases are combined so that they act synergistically to optimize the dielectric gas properties (see Table 2).

Based on Tables 1 and 2 and the data in Fig. 1 it was indicated that a remarkable synergism between N_2 and SF_6 exists and that SF_6/N_2 mixtures constitute a classic example of a multicomponent gaseous insulator (e.g., see [6,7,11,12]). It was thus suggested [11,12] that SF_6/N_2 can constitute a most promising SF_6 substitute. More specifically, Christophorou et al. [11,13] suggested that high pressure (~5–10 atm) N_2 and mixtures of low concentrations (<20%) of SF_6 with N_2 can be used for insulation (GIL), and higher SF_6 concentrations (40–50%) in N_2 can be used for arc quenching and current interruption; they are used in GIL (e.g., see [13,15] and Fig. 2) and other types of electrical equipment. They reduce the amount of SF_6 used and thus they reduce the amount of SF_6 released in the environment.

Table 2
Concept of the multicomponent gaseous dielectric

Two or more gases are combined on the basis of knowledge of their electron–molecule interaction properties to act synergistically to optimize insulation properties

High dielectric strength, V_s, can be effected by combining electron scattering and electron attaching gases, so that one scatters electrons into the energy region where the other picks them up efficiently

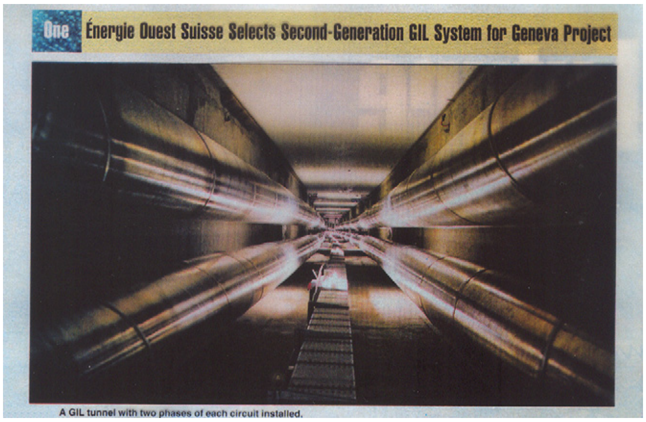

Fig. 2. 300-kV gas-insulated lines (GIL) for electric power transmission located in a tunnel and insulated with 80% N_2 and 20% SF_6 gas mixture [15] as suggested by basic research [7,13].

Clearly, there is a need to develop new environmentally acceptable gaseous dielectrics, especially if GIL is used widely and GIT scale up in numbers. Research in gaseous dielectrics should

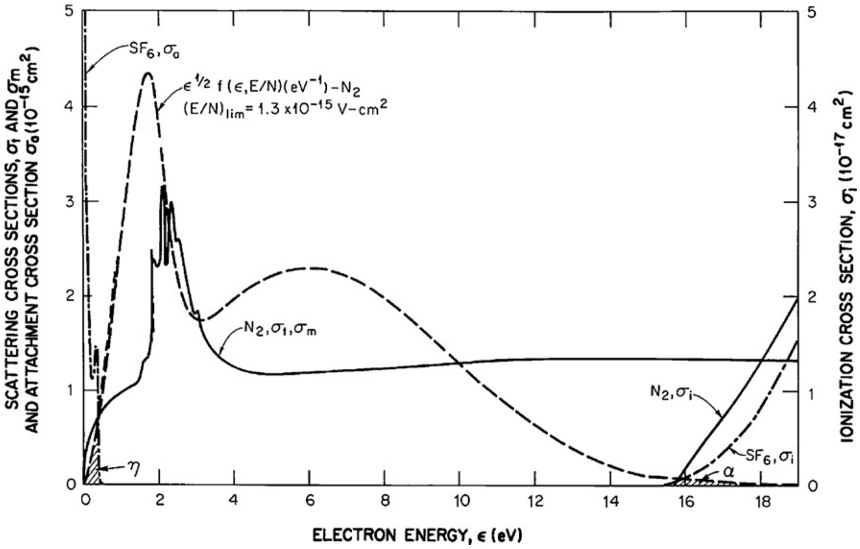

Fig. 1. Total electron-impact ionization cross-section $\sigma_i(\varepsilon)$ for N_2 (—) and SF_6 (– · –) close to the ionization threshold. Total electron scattering cross-section $\sigma_{sc}(\varepsilon)$ for N_2 (—) and total electron attachment cross-section $\sigma_a(\varepsilon)$ for SF_6 (– – –). Electron energy distribution function $f(\varepsilon, E/N)$ in pure N_2 at the limiting value of E/N. The shaded areas designated by η and α are respectively a measure of the electron attachment and electron-impact ionization coefficients for mixtures of N_2 and SF_6 [7].

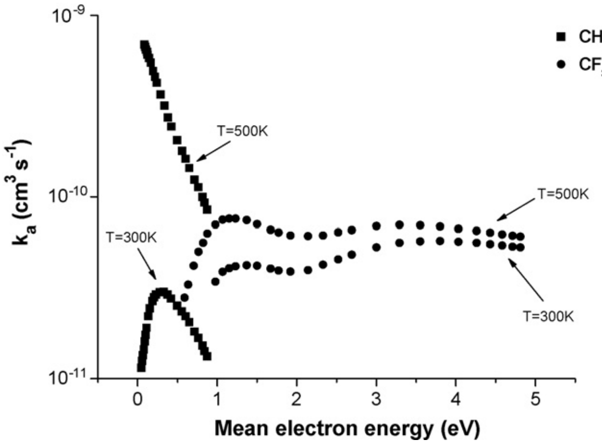

Fig. 3. Total electron attachment rate constants, k_a, for dissociative electron attachment to two environmental halocarbons as a function of the mean electron energy for 300 K and 500 K [18–20].

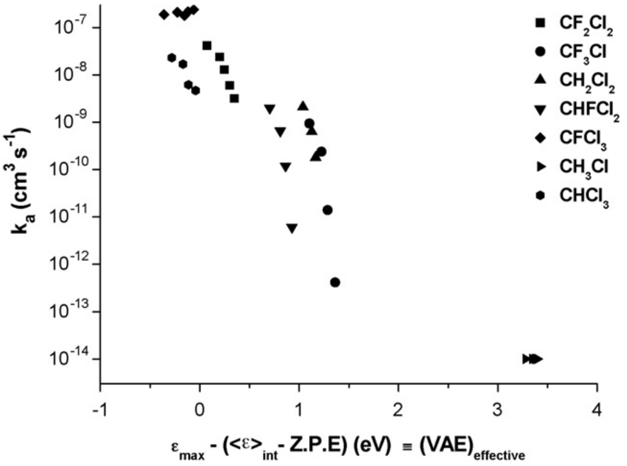

Fig. 4. Total thermal electron attachment rate constants, k_a, for dissociative electron attachment to environmental chlorocarbons as a function of $\varepsilon_{max} - (\langle\varepsilon_{int}\rangle - \mathrm{ZPE})$ (see the text and footnote [23]).

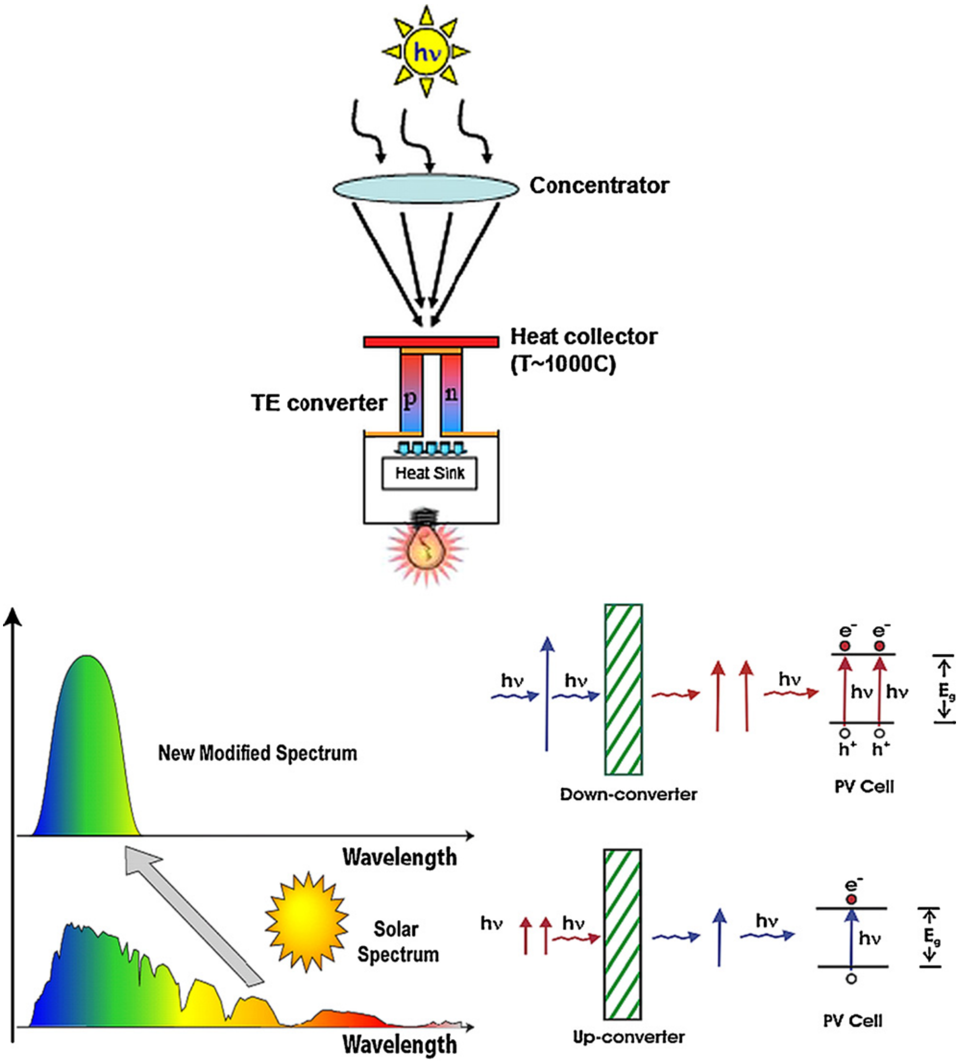

Fig. 5. Schematic representation of the principles of converting sun light or heat to electricity and of shifting the optical frequencies of sun light to regions more suitable for effective conversion of sun light to electricity (from [5]).

be rekindled in view of future energy needs and new energy sources.

3. More efficient destruction of environmental halocarbons by application of knowledge on low-energy electron molecule interactions

Among the methods employed for the destruction of environmental halocarbon molecules in the gas phase are those employing electron-beam-generated plasmas (e.g., non-equilibrium plasmas and various types of discharges; see, for instance, Refs. [1–4]). In these efforts, a key process is

$$e+\mathrm{MX} \rightarrow X^{-}+(M-X) \qquad (1)$$

where MX is the environmental halocarbon molecule, X^- is a negative ion fragment and $(M-X)$ is the complementary radical. Since this process is strongly dependant on electron energy and gas temperature (e.g., see [16–18] and references cited therein), optimization of any method to destruct environmental halocarbons using electrons or plasmas requires quantitative data on the interaction of low-energy electrons (those with kinetic energies between ~0 and ~10 eV) with halocarbon molecules as a function of electron energy ε and gas temperature T (internal energy of the molecule $\langle\varepsilon_{\mathrm{int}}\rangle$).

We wish to emphasize the importance of gas temperature in effecting a more efficient destruction of the halocarbon. This of course depends on the energy dependence of the electron attachment rate constant $k_{\mathrm{a}}(\langle\varepsilon\rangle)$ (see Fig. 3 and data on other molecules in Refs. [1,3,16–22]). For the case of $\mathrm{CH_3Br}$, where the $k_{\mathrm{a}}(\langle\varepsilon\rangle)$ at room temperature peaks at ~0.5 eV the destruction of the halocarbon via (1) can be increased by an order of magnitude via a moderate increase in the gas temperature (300–500 K).

Earlier studies on dissociative electron attachment (e.g., Refs. [21,22]) have shown that the magnitude of the rate constant k_{a} for reaction (1) depends on the energy position ($\langle\varepsilon_{\max}\rangle$) of the electron attaching state of the molecule. When the temperature of the gas is increased, the internal energy ($\langle\varepsilon_{\mathrm{int}}\rangle$) of the molecules is increased and $\langle\varepsilon_{\max}\rangle$ is decreased, that is, the negative ion state can be reached with electrons of lower kinetic energies. This, in turn, effects an increase in the magnitude of k_{a} (e.g., see Refs. [18–20]). This is clearly seen from the data in Fig. 4 where the measured values of the thermal electron attachment rate constant $(k_{\mathrm{a}})_{\mathrm{th}}$ for reaction (1) for several chlorofluorocarbons (see Ref. [18] and sources cited therein) is plotted as a function of $(\varepsilon_{\max}-\langle\varepsilon_{\mathrm{int}}\rangle-\mathrm{ZPE})$, where $\varepsilon_{\max}$ is the energy position of the lowest negative ion resonance [18], $\langle\varepsilon_{\mathrm{int}}\rangle$ is the increase of the internal molecular energy due to the temperature rise calculated from the known vibrational frequencies of these molecules [23], and ZPE is the zero point energy of the molecule (This quantity we designate as the effective vertical electron attachment energy, $\mathrm{VAE_{eff}}$). This finding shows that the halocarbon molecules are decomposed more efficiently with increasing T largely because the electron energy needed to reach the negative ion state is displaced toward lower energies due to the increase of the internal energy of the molecule. The impact of this depends on the value of $\varepsilon_{\max}$.

4. New materials for renewable energy sources

There is an opportunity for the field of electron–molecule interactions to make an impact in energy technologies foremost in new materials for renewable energy sources. This, however, would require quantitative investigations of these processes in the condensed phase and nano-materials both for ground state and for excited [18] molecules. Such areas include those on thermoelectric materials for the conversion of sunlight or of heat (including waste heat) to electricity and optoelectric materials for a more efficient use of solar radiation to generate electricity; for instance, by using a larger section of the spectrum of solar radiation (see Fig. 5 and [5]). As it was pointed out in Ref. [5], the ability to pattern and control nanoscale matter presents unique opportunities for developing new materials, for instance, for solar energy conversion. Knowledge of the electron transport and loss processes and of the electrical breakdown properties of such matter is clearly significant.

References

[1] L.G. Christophorou, S.R. Hunter, in: L.G. Christophorou (Ed.), Electron–Molecule Interactions and Their Applications, vol. 2, Academic Press Inc., New York, 1984 (Chapter 5).

[2] B.M. Penetrante, S.E. Schultheis, Non-thermal Plasma Techniques for Pollution Control. NATOASI Series G, Ecological Sciences, vol. 34, Part A, NATO, 1993.

[3] L.G. Christophorou, J.K. Olthoff, Fundamental Electron Interactions with Plasma Processing Gases, Springer, New York, 2004.

[4] R.C. Slater, D.H. Douglas-Hamilton, J. Appl. Phys. 52 (1981) 5820;
L. Bromberg, D.R. Cohn, M. Koch, R.M. Patrick, P. Thomas, Phys. Lett. A 173 (1993) 293;
M. Kock, D.R. Cohn, R.W. Patrick, M.P. Schuetze, L. Bromberg, D. Reilly, K. Hadidi, P. Thomas, P. Falkos, Environ. Sci. Technol. 29 (1995) 2946;
E.M. Van Veldhuizen (Ed.), Electrical Discharges for Environmental Purposes—Fundamentals and Applications, Nova Science, Huntington, NY, 2000;
Y.-S. Won, D.-H. Han, T. Stuchinskaya, W.-S. Park, H.-S. Lee, Radiat. Phys. Chem. 63 (2002) 165;
L.A. Rosocha, IEEE Trans. Plasma Sci. 1–9 (2005).

[5] USA DOE, 2005, http://www.sc.doe.gov/bes/reports/abstracts.html#SEU.

[6] L.G. Christophorou, Proceedings of the XIIIth International Conference on Phenomena in Ionized Gases Invited Lectures, VEB Export Import, Leibzig, East Germany, 1977, p. 51.

[7] L.G. Christophorou, Nucl. Instrum. Methods Phys. Res. 268A (1988) 424.

[8] L.G. Christophorou, I. Sauers, D.R. James, H. Rodrigo, M.O. Pace, J.G. Carter, S.R. Hunter, IEEE Trans. Electr. Insul. EI-19 (1984) 550.

[9] L.G. Christophorou (Ed.), Gaseous Dielectrics, vol. I, Oak Ridge National Laboratory Report CONF-780301, 1978;
L.G. Christophorou (Ed.), Gaseous Dielectrics, vol. II, Pergamon Press, New York, 1980;
L.G. Christophorou (Ed.), Gaseous Dielectrics, vol. III, Pergamon Press, New York, 1982;
L.G. Christophorou, M.O. Pace (Eds.), Gaseous Dielectrics, vol. IV, Pergamon Press, New York, 1984;
L.G. Christophorou, D.W. Bouldin (Eds.), Gaseous Dielectrics, vol. V, Pergamon Press, New York, 1987;
L.G. Christophorou, I. Sauers (Eds.), Gaseous Dielectrics, vol. VI, Plenum Press, New York, 1990;
L.G. Christophorou, D.R. James (Eds.), Gaseous Dielectrics, vol. VII, Plenum Press, New York, 1994;
L.G. Christophorou, J.K. Olthoff (Eds.), Gaseous Dielectrics, vol. VIII, Kluwer Academic/Plenum Publishers, New York, 1998;
L.G. Christophorou, J.K. Olthoff (Eds.), Gaseous Dielectrics, vol. IX, Kluwer Academic/Plenum Publishers, New York, 2001;
L.G. Christophorou, J.K. Olthoff, P. Vassiliou (Eds.), Gaseous Dielectrics, vol. X, Springer, New York, 2004.

[10] Electric Power Research Institute Report EPRI-EL-2620. (Prepared by R.E. Wootton et al. of the Westinghouse Electric Corporation), 1982.

[11] L.G. Christophorou, R.J. Van Brunt, IEEE Trans. Dielectr. Electr. Insul. 2 (1995) 952.

[12] L.G. Christophorou, R.J. Van Brunt, $\mathrm{SF_6}$ Insulation: Possible Greenhouse Problems and Solutions, National Institute of Standards and Technology, NISTIR 5685, 1995.

[13] L.G. Christophorou, J.K. Olthoff, D.S. Green, National Institute of Standards and Technology, NIST Technical Note 1425, November 1997.

[14] Intergovernmental Panel on Climate Change (IPCC), The 1994 Report of the Scientific Assessment Working Group of IPCC.

[15] J. Riedl, T. Hillers, IEEE Power Engineering Review, September 2000, p. 15; J. Riedl, T. Hillers, Transmission and Distribution World, January 2001, p. 30.

[16] L.G. Christophorou (Ed.), Electron–Molecule Interactions and their Applications, vols. 1–2, Academic Press, New York, 1984.

[17] L.G. Christophorou, Z. Phys. Chem. 195 (1997) 195.

[18] L.G. Christophorou, J.K. Olthoff, Adv. At. Mol. Opt. Phys. 44 (2000) 155.

[19] P.G. Datskos, L.G. Christophorou, J.G. Carter, J. Chem. Phys. 97 (1992) 9031.

[20] S.M. Spyrou, L.G. Christophorou, J. Chem. Phys. 82 (1985) 2620.

[21] L.G. Christophorou, Atomic and Molecular Radiation Physics, Wiley-Interscience, New York, 1971.
[22] L.G. Christophorou, D.L. McCorkle, A.A. Christodoulides, in: Electron-Molecule Interactions and Their Applications, vol.1, Academic Press Inc., New York, 1984 (Chapter 6).
[23] The quantity $<\varepsilon_{\mathrm{int}}>$ was determined using the formula $<\varepsilon_{\mathrm{int}}> = \sum (h\nu/(e^{h\nu/kT} - 1)$ and the frequencies listed by T. Shimanouchi, Tables of Molecular Vibrational Frequencies consolidated Volume I, National Bureau of Standards, 1972, except for $CHFCl_2$ where the frequencies were used were taken from M. Snels and M. Quack, J. Chem. Phys. 95 (1991) 6355.