POSSIBILITY OF LASER ASYMMETRIC SYNTHESIS OF HYDROGEN PEROXIDE MOLECULE ENANTIOMERS FROM A RACEMIC MIXTURE WITHOUT PRELIMINARY MOLECULAR ORIENTATION

Yu. V. Vladimirova, B. A. Grishanin, D. V Zhdanov, V. N. Zadkov, and H. Takahashi*

E-mail: grishan@comsim1.phys.msu.ru

Using hydrogen peroxide as an example, the specific features of the laser control of the chiral state of an initially racemic mixture of molecules without their preliminary orientation have been studied. The determining role of molecular rotations and the molecular ensemble temperature have been revealed, and promising schemes for the laser asymmetric synthesis of enantiomers from a racemic mixture have been proposed.

INTRODUCTION

Chirality is a property of an object of being incapable of coinciding with its mirror image. Simplest examples of chiral objects are the left and the right hand of man, keys, screws, and so on. Accordingly, the notion of molecular chirality is associated with the existence of different configurations of one and the same molecule that are mirror images of each other. The molecules forming such a pair are chiral, and the corresponding molecular configurations are referred to as the "right" (D) and "left" (L) enantiomers.

Two aspects associated with chiral molecules have aroused special interest today. One aspect is the phenomenon of mirror symmetry violation in the bioorganic world that has not yet been figured out. The other aspect is conditioned by the problems of asymmetric synthesis and effective separation of racemic mixtures and is associated with the search for methods of controlling the chiral states of molecules.

Chemical and biochemical methods have traditionally been the main means to control the chiral states of molecules. There are examples of successful use of these methods for the purposes of chemical asymmetric synthesis of various compounds, and effective methods have been developed to separate racemic mixtures. However, a common shortcoming of such methods is the fact that an inventive solution of a laborious problem is required in each particular case.

As demonstrated by the pertinent investigations, it is only optical methods out of the entire arsenal of physical means that make it possible to reliably determine and distinguish the enantiomers of chiral molecules. Therefore, optical methods, those of laser physics in particular, can be effectively used not only to diagnose chiral molecular states, but to control them as well. [1–7].

The present work considers the physical mechanisms underlying the control of chiral states of hydrogen peroxide (H_2O_2) molecules in an originally racemic mixture within the framework of our previously developed concept of controlling the chiral states of molecules by means of noncomplanar laser field configurations [8]. A new scheme is suggested here for the laser asymmetric synthesis of enantiomers of hydrogen peroxide molecules from a racemic mixture without their preliminary orientation.

---

* Faculty of Chemistry, Waseda University, Tokyo 169-8555, Japan.

HYDROGEN PEROXIDE—THE SIMPLEST CHIRAL MOLECULE

The H_2O_2 molecule (Fig. 1) is the simplest chiral molecule whose geometry is noninvariant under the $(x', y', z') \rightarrow (x', -y', z')$ transformation of any rectangular coordinate system. Following this transformation, the initial position of the molecule's atoms cannot be restored by the rotation operation. We select the $\{x', y', z'\}$ coordinate system related to the molecule such that the z'-axis passes through the oxygen molecules and the $x'z'$-plane, through the bisectrix of the angle $\theta = \angle HOOH$ (see Fig. 1). The choice of the z'-axis direction enables us to assign a certain sense to the angle of torsion, θ, so as to associate the left enantiomer with $\theta > 0$ and the right one, with $\theta < 0$.
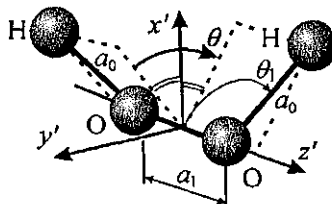

Fig. 1

Geometry of the H_2O_2 molecule and the x', y', z' coordinate system rigidly fixed to it. The angle of torsion, θ, is the dihedral angle formed by the two OOH planes. Correspondent to the ground state are $\theta = 112.5°$, $\theta_1 = 99°$, $a_1 = 1.451$ Å, $a_0 = 0.962$ Å [13].

According to theoretical calculations and experimental data [9–12], the relationship between the potential energy of the molecule's ground-state and the torsional (or so-called reaction) coordinate θ has the form of a symmetric double-well potential with the *cis-* and *trans*-barrier heights of 2460 and 386 cm^{-1}, respectively, and the θ minimum points around 110–120°. The energy eigenstates of the molecule are split into doublets consisting of the $|S_i\rangle$ and $|A_i\rangle$ states symmetric and antisymmetric with respect to θ, respectively.

For small inorganic molecules like H_2O_2, the time of tunneling through the *trans*-barrier, τ_{tun}, is, as a rule, short, and so the doublet splitting is sufficiently great and, as a consequence, the D- and L-enantiomers of such molecules are unstable, turning one into the other all the time. The molecular chirality in molecules of this type is called dynamical (or oscillating).

In the hydrogen peroxide molecule, the energy splitting between the lower doublet states $|S_0\rangle$ and $|A_0\rangle$ is $\Delta\omega_{AS}^{(0)} = 11.4$ cm^{-1} that corresponds to $\tau_{\text{tun}}^{(0)} = 2.9$ ps. This time grows longer rapidly as the molecule moves to higher torsional states and changes substantially upon excitation of other vibrational modes in the molecule. The latter include the deformation modes ν_1 and ν_5 corresponding to the longitudinal vibrations of the O–H bonds and the stretching mode ν_2 associated with the variation of the angles $\angle OOH$. The states corresponding to the lowermost excitations of these modes are those with the torsional doublet splittings $\Delta\omega_{AS}^{(\nu_1)} = 8.2$ cm^{-1}, $\Delta\omega_{AS}^{(\nu_5)} = 8.1$ cm^{-1}, and $\Delta\omega_{AS}^{(\nu_2)} = 2.4$ cm^{-1}. Some characteristics of the corresponding vibrational transitions calculated in [13] are presented in Table 1. The thermal population of these excited states under normal conditions ($T \cong 200$ cm^{-1}) can be disregarded. We note that the resonant dipole excitation of the torsional modes can only be effected by means of pulses whose frequencies lie in the far-IR range, and so it is difficult to achieve.

The difference in mass between the O and H atoms being great, one can take it to a good accuracy that the principal axes of inertia in the H_2O_2 molecule coincide with the x'-, y'-, and z'-axes in Fig. 1, with the principal moments of inertia satisfying the relations $I_{x'}, I_{y'} \gg I_{z'}$, $I_{x'} \cong I_{y'}$ at that. For this reason, we can use the simplified methods described below to account for rotational motion for states with small moments of momentum, J.

1. Symmetric top approximation where we approximately put $I_{x'} = I_{y'} = I$. The pertinent estimates have shown that the errors introduced in this case for the lower rotational states with $J < 4$ do not exceed a few tenths of a percent, and so this approximation is accurate enough.

2. One-dimensional reduction of rotations. We disregard the rotation of the oxygen atoms, i. e., we assume that the direction of the z'-axis is specified by the fixed angles φ and γ relative to the rest coordinate

Table 1

Main Characteristics of Transitions

Vibrational transition $(X, Y = S, A;\ X \neq Y)$	Transition frequency (cm^{-1}) in $\{x', y', z'\}$ system	Dipole moment directions
$|X_{\nu_0}\rangle \Leftrightarrow |Y_{\nu_1}\rangle$	3610	$\{1, 0, 0\}$
$|X_{\nu_0}\rangle \Leftrightarrow |X_{\nu_5}\rangle$	3611	$\{0, 1, 0\}$
$|X_{\nu_0}\rangle \Leftrightarrow |X_{\nu_5}\rangle$	3611	$\{0, 0, 1\}$
$|X_{\nu_1}\rangle \Leftrightarrow |Y_{\nu_2}\rangle$	2213	$\{1, 0, 0\}$
$|X_{\nu_0}\rangle \Leftrightarrow |Y_{\nu_2}\rangle$	1396	$\{1, 0, 0\}$

system x, y, z. In that case, the problem of molecular rotations reduces to a unidimensional problem with the angle θ between the x'-axis and the xz'-plane acting as the rotational coordinate. The expressions for the rotational eigenstates assume the form

$$|J_A\rangle = \frac{1}{\sqrt{\pi}}\sin(J\tilde{\theta}), \quad |J_S\rangle = \begin{cases} \dfrac{1}{\sqrt{2\pi}} & \text{at } J = 0, \\ \dfrac{1}{\sqrt{\pi}}\cos(J\tilde{\theta}) & \text{at } J > 0. \end{cases} \tag{1}$$

We note that for all of the excitations of interest, the vibrational and rotational degrees of freedom of the molecule can be considered independent.

SCENARIO OF LASER ASYMMETRIC SYNTHESIS OF THE H_2O_2 MOLECULE ENANTIOMERS FROM A RACEMIC MIXTURE

Let us consider the possibility of controlling the chiral states of the H_2O_2 molecule by means of a number of linearly polarized picosecond laser pulses $\mathbf{E}_k = \epsilon_k A_k(t)\cos(\omega_k t + \varphi_k)$ with frequencies ω_k in the near-IR region that excite in a resonant manner a sequence of vibrational-rotational dipole transitions in the molecule. The states corresponding to the left and right configurations of the molecule have the form

$$|L_i\rangle = \frac{1}{\sqrt{2}}(|S_i\rangle + |A_i\rangle), \quad |D_i\rangle = \frac{1}{\sqrt{2}}(|S_i\rangle - |A_i\rangle). \tag{2}$$

It was proved in [8, 14] that the necessary condition for the laser asymmetric synthesis of enantiomers in the case of an arbitrarily oriented molecule is the use of laser fields with noncomplanar polarization vectors such that the field polarity inversion should cause excitation of chiral states of the opposite sense. It is exactly this requirement that determines the minimal necessary number of fields, equal to three, in the laser distillation scenario (scheme). To induce chiral molecular states it is necessary that the torsional doublets be coupled in a coherent fashion through a sequence of transitions via intermediate states. Simple analysis shows that in the case of nonoriented molecules the number of such transitions should certainly be odd. Besides, if n_α is the number of resonant fields in this sequence, whose polarization vectors lie in a certain plane α, while the polarization vectors of the rest $n_\perp$ fields of the sequence are orthogonal to it, then $n_\perp$ should be odd.

The simplest scenario of the laser asymmetric synthesis of enantiomers of the H_2O_2 molecule from a racemic mixture implemented by means of a sequence of three laser pulses is illustrated in Fig. 2. The use of rotational sublevels of the ground state as various intermediate levels in the sequence of transitions in this scheme has made it possible to reduce the number of acting laser pulses to the minimum possible value equal to three.

Let us demonstrate the operability of the given scheme for a model ensemble of randomly oriented H_2O_2 molecules in the unidimensional rotation reduction approximation. To simplify calculations the ground state of the molecules is taken to be the stationary state at zero rotational temperature $(J = 0)$, where the only populated vibrational sublevel is the lower torsional doublet described by the density matrix

$$\hat{\rho}_0 = (1/\sqrt{2})\,(|S_0\rangle\,\langle S_0| + |A_0\rangle\,\langle A_0|). \tag{3}$$
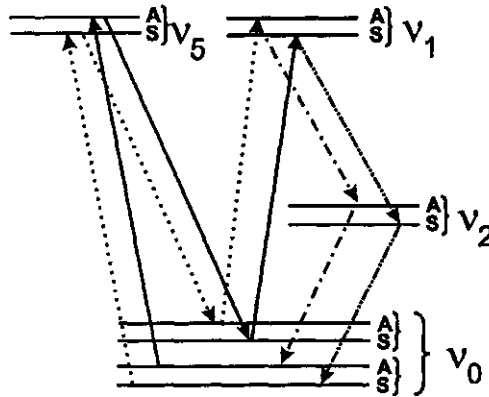
Fig. 2

Schematic diagram of induced laser transitions in the scenario of laser asymmetric synthesis of H_2O_2 molecule enantiomers from a racemic mixture. The arrows indicate the transitions induced by different laser pulses.

Then we assume that the laser pulses in the excitation scheme do not overlap and disregard the relaxation processes and nonresonance transitions. Transitions are considered to be of resonance character if their detuning from the laser field frequency does not exceed 30 cm^{-1} (for this to hold true, the pulses should not be shorter than picosecond ones). We then can assume that it is only the levels with $J < 2$ that are involved in the interaction. Therefore, the dynamics of the processes can be described in the rotating wave approximation in the 24-level basis $|S_{\nu_i}\rangle |0_S\rangle, |A_{\nu_i}\rangle |0_S\rangle, |S\rangle_{\nu_i} |1_S\rangle, |A_{\nu_i}\rangle |1_S\rangle, |S_{\nu_i}\rangle |1_A\rangle, |A_{\nu_i}\rangle |1_A\rangle\}$, where i consecutively assumes the values $0, 2, 5$ and 1.

Calculation has shown that such laser action in the initially racemic mixture of chiral molecules a degree of chirality of χ_{ν_0} or χ_{ν_2} for the molecules in the vibrational ground state ν_0 or in the vibrationally excited state ν_2, respectively. Since $\Delta\omega_{AS}^{(\nu_0)} \neq \Delta\omega_{AS}^{(\nu_2)}$, the degree of chirality of the medium as a whole also becomes other than zero. If we introduce the notation

$$\Upsilon_{1,1}(\varphi,\gamma) = \frac{1}{\hbar\sqrt{2}} \langle X_{\nu_0}| \epsilon_1, \hat{d} |X_{\nu_1}\rangle, \quad \Upsilon_{1,2}(\varphi,\gamma) = \frac{1}{\hbar\sqrt{2}} \langle X_{\nu_0}| \epsilon_1, \hat{d} |Y_{\nu_5}\rangle, \quad \Upsilon_{1,3}(\varphi,\gamma) = \langle X_{\nu_0}| \epsilon_1, \hat{d} |X_{\nu_5}\rangle,$$

$$\Upsilon_2(\varphi,\gamma) = \frac{1}{\hbar\sqrt{2}} \langle X_{\nu_1}| \epsilon_2, \hat{d}) |X_{\nu_2}\rangle, \quad \Upsilon_3(\varphi,\gamma) = \frac{1}{\hbar\sqrt{2}} \langle X_{\nu_0}| \epsilon_3, \hat{d} |X_{\nu_2}\rangle, \tag{4}$$

$$\Psi_1(\varphi,\gamma) = \sqrt{\Upsilon_{1,1}^4 + 16\Upsilon_{1,2}^2\Upsilon_{1,3}^2}, \quad \Psi_2(\varphi,\gamma) = \Upsilon_{1,1}^2 + 2\Upsilon_{1,2}^2 + 2\Upsilon_{1,3}^2, \quad \mathcal{S}_j = \int \frac{A_j(t)}{2} dt,$$

where $X, Y = S, A$, $X \neq Y$, then, considering (1), (2) and (3), the expressions for the degree of chirality are represented in the form

$$\chi_{\nu_0}(\varphi,\gamma) = \frac{\chi_0}{2} \cos(2\pi\Delta\omega_{AS}^{\nu_0} t + \varphi_0), \quad \chi_{\nu_2}(\varphi,\gamma) = -\frac{\chi_0}{2} \cos(2\pi\Delta\omega_{AS}^{\nu_2} t + \varphi_0),$$

$$\chi(\varphi,\gamma) = -\chi_0 \sin(\pi(\Delta\omega_{AS}^{\nu_0} + \Delta\omega_{AS}^{\nu_2})t) \sin(\pi(\Delta\omega_{AS}^{\nu_0} - \Delta\omega_{AS}^{\nu_2})t), \tag{5}$$

where

$$\chi_0(\varphi,\gamma) = 4\, \Upsilon_{1,1}\Upsilon_{1,2}\Upsilon_{1,3}$$
$$\times \left[\sin\frac{\mathcal{S}_1\sqrt{\Psi_2 - \Psi_1}}{\sqrt{2}} \sqrt{\Psi_1 + \Psi_2}(\Psi_1 - \Upsilon_{1,1}^2) + \sin\frac{\mathcal{S}_1\sqrt{\Psi_1 + \Psi_2}}{\sqrt{2}} \sqrt{\Psi_2 - \Psi_1}(\Upsilon_{1,1}^2 + \Psi_1) \right]$$
$$\times \left[\sqrt{2}\Psi_1^2\sqrt{\Psi_2^2 - \Psi_1^2} \right]^{-1} \sin(\mathcal{S}_2\Upsilon_2)\sin(2\mathcal{S}_3\Upsilon_3) \left(\cos\frac{\mathcal{S}_1\sqrt{\Psi_2 - \Psi_1}}{\sqrt{2}} - \cos\frac{\mathcal{S}_1\sqrt{\Psi_1 + \Psi_2}}{\sqrt{2}} \right)$$
$$\times \sin(\varphi_1 - \varphi_2 - \varphi_3) \tag{6}$$

is the oscillation amplitude (of arbitrary sign in the general case) of the degree of chirality. The latter attains its maximum of $\chi_0 = 0.85$ with the z'-axis orientation corresponding to $\varphi_1 - \varphi_2 - \varphi_3 = \pi/2$, $\mathcal{S}_2 \Upsilon_2 = \pi/2$, $\mathcal{S}_3 \Upsilon_3 = \pi/4$, $\mathcal{S}_1 \Upsilon_{1,1} = 1.22$, $\mathcal{S}_1 \Upsilon_{1,2} = 1.19$, $\mathcal{S}_1 \Upsilon_{1,3} = 1.19$.

These estimates suggest that for partially oriented molecules the scheme presented here is practically no less efficient than the schemes proposed in [1–7] for preliminarily oriented molecules. The distinction of the given scheme is that $\langle \chi_0 \rangle \neq 0$ when averaging over all of the possible orientations of the z'-axis. The average amplitude $\langle \chi_0 \rangle = 0.23$ corresponds to the mutually orthogonal polarizations of the pumping pulses (i. e., their maximal noncomplanarity) with the parameters $\mathcal{S}_1 = 6.02 \times 10^{-4}$ V s m^{-1}, $\mathcal{S}_2 = 1.39 \times 10^{-2}$ V s m^{-1}, $\mathcal{S}_3 = 4.49 \times 10^{-4}$ V s m^{-1}, $\varphi_1 - \varphi_2 - \varphi_3 = \pi/2$.

The results of calculation of the oscillation amplitude of the degree of chirality presented in Fig. 3 show that, at the values of the parameters used, the sign of the amplitude of the induced degree of chirality χ_0 is always positive, no matter what the orientation of the molecule. We note that the results of more accurate calculations made by us using the symmetric top model coincide in the order of magnitude with those presented here.
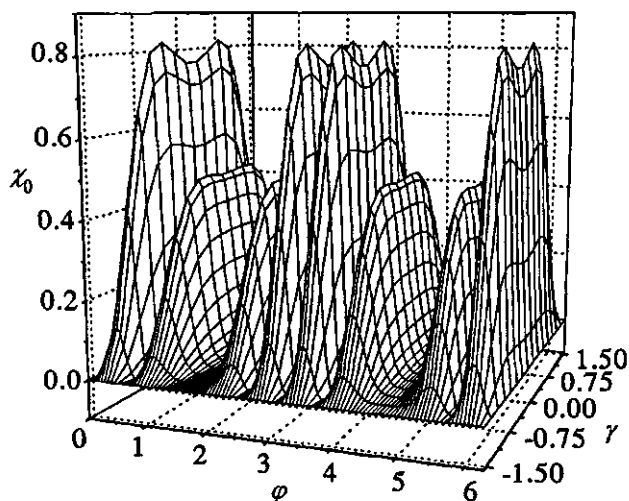

Fig. 3

Induced chirality amplitude χ_0 as a function of angles φ, γ specifying the molecule's spatial orientation in the model with the unidimensional rotation reduction approximation.

The calculation presented graphically demonstrates that the scenario suggested for the laser asymmetric synthesis of enantiomers from a racemic mixture is also operable in the case of nonoriented molecules, at least for initial conditions (3), i. e., at zero rotational temperature of the molecules in the mixture. Such a situation can be experimentally realized in a supersonic molecular jet originating when gas molecules flow from a container into a vacuum reservoir. Owing to adiabatic expansion processes, the rotational degrees of freedom of molecules in such a jet become strongly "frozen", with their rotational temperature T_{rot} being reduced to a few kelvins [15, 16].

The rise of the rotational temperature of the molecules results in a considerable increase of the role of the rotational-torsional off-resonance detuning and the excitation of a great number of rotational states with which the laser pulses practically fail to interact. This naturally reduces the effect of separation of the racemic mixture. Therefore, when considering the scenario of laser asymmetric synthesis for initial conditions with a high T_{rot} corresponding, for example, to the saturated H_2O_2 vapor under normal conditions, it is necessary to account for rotations more accurately. Calculations were carried out with due account for rotations on the basis of the symmetric top model. When using pulses with durations of ~ 1 ps, one can select their frequencies so that it is only the levels with $J < 3$ that will be involved in the dynamics. The calculation corresponding to this case estimates at $\sim 10^{-3}$ the orientation-averaged local oscillation amplitude of the degree of chirality induced by mutually orthogonal pulses with intensities of $\sim 10^{12}$ W/cm^2.

It is important to note that in spite of the strong negative effect of rotations on the efficiency of the scheme, it is exactly the presence of rotational splitting that has made it possible to use the rotational sublevels of the ground state as various intermediate states in the necessary sequence of transitions.

Thus, under normal conditions the method suggested here also seems effective enough and can experimentally be implemented in the saturated H_2O_2 vapor. In this case, the three laser pulses induce a space distribution of the degree of chirality in the form of a three-dimensional lattice in a region with characteristic size ~ 1 mm^3. As a result of the linear quadrupole interaction of the nonracemic medium with the tail of the last of the pulses of the scheme, there develops a response pulse with a certain polarization and a propagation direction other than that of the last pulse of the scheme. The corresponding response pulse intensity is in this case estimated at 10^{-8} W/cm^2.

CONCLUSIONS

Therefore, using the enantiomers of the H_2O_2 molecule as an example, we have demonstrated the possibility of controlling the chiral states of molecules and suggested a scenario of laser asymmetric synthesis of enantiomers from a racemic mixture of molecules without their preliminary orientation. The estimates of the magnitude of the signal recorded allow one to expect that it will be possible to detect the results of laser asymmetric synthesis, especially in conditions of experiments with "frozen" rotational degrees of freedom of the molecules, for example, in a supersonic molecular jet. The possibility of purposeful utilization of rotational degrees of freedom of the molecules allows one to reduce the necessary number of pulses in the laser synthesis scheme and to partially offset the negative effect of rotational dephasing. This inspires hope that it will prove possible to register the effect using the linear response of the medium in experiments with the saturated H_2O_2 vapor under normal conditions as well.

REFERENCES

1. L. Gonzàlez, K. Hoki, D. Kröner, et al., *J. Chem. Phys.*, vol. 113, no. 24, p. 11134, 2000.
2. A.S. Leal, D. Kröner, and L. Gonzàlez, *Eur. Phys. J. D*, vol. 14, p,. 185, 2001.
3. M. Shapiro, E. Frishman, and P. Brumer, *Phys. Rev. Lett.*, vol. 84, no. 8, p. 1669, 2000.
4. P. Brumer, E. Frishman, and M. Shapiro, *Phys. Rev. A*, vol. 65, p. 015401, 2001.
5. L. Gonzàlez, D. Kröner, and I.R. Sola, *J. Chem. Phys.*, vol. 115, no. 6, p. 2519, 2001.
6. K. Hoki, L. Gonzàlez, and Y. Fujimura, *J. Chem. Phys.*, vol. 116, no. 20, p. 8799, 2002.
7. Y. Ohta, K. Hoki, and Y. Fujimura, *J. Chem. Phys.*, vol. 116, no. 27, p. 7509, 2002.
8. S.S. Bychkov, B.A. Grishanin, and V.N. Zadkov, *Zh. Eksp. Teor. Fiz.*, vol. 116, no. 7, p. 31, 2001.
9. Y. Amako and P.A. Goguère, *Can. J. Chem.*, vol. 40, p. 765, 1962.
10. R.L. Redington, W.B. Olson, and P.C. Gross, *J. Chem. Phys.*, vol. 36, p. 1311, 1962.
11. W.R. Busing and H.A. Levy, *J. Chem. Phys.*, vol. 42, p. 3054, 1965.
12. V.I. Tyulin, P.A.L. Bachi-Tom, and V.K. Matveev, *Vestn. Mosk. Univ. Khimiya*, vol. 39, no. 2, p. 75, 1998.
13. J. Koput, S. Carter, and N.C. Handy, *J. Chem. Phys.*, vol. 115, no. 18, p. 8345, 2001.
14. E. Frishman, M. Shapiro, D. Gerbasi, et al., *J. Chem. Phys.*, vol. 119, no. 14, p. 7238, 2003.
15. R. Campargue, *Atomic and Molecular Beams: The State of the Art 2000*, Berlin, 2001.
16. R. Fausto, ed., *Low Temperature Molecular Spectroscopy Proceedings of the NATO Advanced Study Institute*, Nato Science Series C, vol. 483, Kluwer Academic Publishers, 1996.

10 November 2004   Department of General Physics and Wave Processes