Reduced Two-Level Approach for Air Kinetics in Recombination Regime

Gianpiero Colonna[*], Lucia Daniela Pietanza[†] and Mario Capitelli[**]

[*]*CNR-IMIP, sede di Bari, Via Amendola 122/D, 70126, Bari, Italy, e-mail: gianpiero.colonna@ba.imip.cnr.it*
[†]*CNR-IMIP, sede di Bari, Via Amendola 122/D, 70126, Bari, Italy, e-mail: daniela.pietanza@ba.imip.cnr.it*
[**]*Dipartimento di Chimica, Universitá di Bari, Via Orabona, 4, 70126, Bari, Italy, e-mail: mario.capitelli@ba.imip.cnr.it*

Abstract. The possibility of using reduced model, that account for non–Boltzmann vibrational distributions for nitrogen monoxide kinetics has been explored. The basic idea is that the rate coefficients, which are proportional to the tail of the vibrational distribution function, are strictly correlated to reactant density rather than to vibrational temperature, which depend on the low energy distribution. The model consider the rate coefficients as a function of the population of the last vibrational level of the relevant species, which evolution is calculated with a proper kinetic equation.

Keywords: state-to-state kinetics

INTRODUCTION

To model the expansion of high enthalpy flows, it is necessary to consider thermo-chemical nonequilibrium. A very accurate approach is the so called *state–to–state* (STS) model [1, 2] that describes the evolution of any internal state relevant for the considered species. This model requires considerable numerical efforts, which limits its applicability to low dimensional systems (1D or 2D). Moreover, the data set (state–selective rates) is quite scanty, and must be completed by interpolation or, worse, extrapolation procedures, reducing the accuracy. On the other hand, the multi-temperature (MT) model [3], which defines a different temperature for each degree of freedom, is commonly used, requiring limited additional computational resources, but, differently from state–to–state approach, the distributions are supposed to follow the Boltzmann shape, having temperature different from the translational one. In supersonic expansion of molecular gases through converging-diverging nozzles, the atomic recombination overpopulates the distribution tails, resulting in non-Boltzmann distributions. This effect reflects on the rate coefficients of exothermal chemical processes such as dissociation or NO formation [1, 2].

In the past years we have investigated the possibility of using a reduced model that accounts for the non-Boltzmann distributions for the pure nitrogen system [4]. The basic idea is that the rate coefficients, which are proportional to the tail of the vibrational distribution function, are strictly correlated to atomic density rather than to vibrational temperature, which describe only the low energy distribution. The model has been further improved relating the rates of molecular dissociation to the population of the last vibrational level [5], closing the system with a kinetic equation for the population of the last vibrational level. We will refer to this approach as *Two–Level Distribution* (TLD) model.

In this work, the TLD model has been extended to the air mixture, introducing a complex interplay between the distributions of the different species (N_2, O_2) [1, 2].

MODEL DESCRIPTION

In this paper we will compare the results obtained by the STS model with those obtained with the MT and the TLD models in 5 species air (N_2, N, O_2, O, NO). In this section we will briefly describe these models.

State-to-state model

The STS model considers the processes in tab. 1. The kinetic model is not complete because the mixed processes, as vT for N_2 by oxygen, have been neglected, even if their contribution can be important.

TABLE 1. Processes considered in the state–to–state model.

$N_2(v)+N_2 \rightleftharpoons N_2(v-1)+N_2$	$N_2(v)+N \rightleftharpoons N_2(v-\Delta v)+N$	$N_2(v)+N_2(w-1) \rightleftharpoons N_2(v-1)+N_2(w)$
$N_2(v)+N_2 \rightleftharpoons 2N+N_2$	$N_2(v)+N \rightleftharpoons 2N+N$	$O_2(v)+O_2 \rightleftharpoons O_2(v-1)+O_2$
$O_2(v)+O \rightleftharpoons O_2(v-\Delta v)+O$	$O_2(v)+O_2(w-1) \rightleftharpoons O_2(v-1)+O_2(w)$	$O_2(v)+O_2 \rightleftharpoons 2O+O_2$
$O_2(v)+O \rightleftharpoons 2O+O$	$N_2(v)+O \rightleftharpoons NO+N$	$O_2(v)+N \rightleftharpoons NO+O$

For the Zel'dovich reactions (NO formation), the rate coefficients have been taken from the works of Bose and Candler [6, 7]. The vT and dissociation by atoms are those calculated by Esposito [8, 9]. The dissociation rate by molecules have been calculated considering the same dependence on the vibrational quantum number of the dissociation by atoms, normalized to reproduce the thermal rates reported by Shatalov [10].

Multi–temperature model

The multi–temperature model considers, for each species S, the relaxation equation of the vibrational energy

$$\frac{dE_S^{vib}(T_{v,S})}{dt} = P\frac{E_S^{vib}(T) - E_S^{vib}(T_{v,S})}{p\tau} \tag{1}$$

where P is the pressure and using the $P\tau$'s reported in ref. [3] and.

The rates of chemical processes (dissociation, NO formation) are calculated summing the state–to–state rates ($K_{S,v}^p$) over a Boltzmann vibrational distributions, namely $n_{S,v}^B$, as

$$K_S^0 = \sum_{v=0}^{V_{max}} n_{S,v}^B(T_{v,S})K_{S,v}^p(T) \tag{2}$$

The rate of the reverse processes, that does not depend on the distributions, it is calculated as the sum over the state–to–state recombination rates,

$$K_S^{rev} = \sum_{v=0}^{V_{max}} K_{S,v}^{rev}(T) \tag{3}$$

where K^{rev} were obtained from K^p applying the detailed balance principle. In this way the state–to–state and multi–temperature models are based on coherent data sets.

Two-Level Distribution Model

This model considers as relevant quantities for the rate coefficients the vibrational temperature, the population of the last vibrational level of diatomic molecules and the gas temperature [4, 5].

The population of the last level α_S of the S–th species is obtained by solving a master equation just for this level, considering gains and losses coming from chemical processes, such as dissociation or NO reactions, and the losses due to vT, being the vv and the vT up–pumping negligible in recombination regime [4, 5]. In this way we have a quantity $(T_{v,S})$ representing the low energy distribution and one (α_S) representing the high level distribution.

The model for the N_2 dissociation rate has been already described in ref. [5], considering the rate coefficients as the sum of two contributions

$$K_S^{diss} = K_S^0(T, T_{v,S}) + K_S^1(T, \alpha_S) \tag{4}$$

where K^0 is the two–temperature rate as reported in eq. 2 and $K_S^1(T, \alpha_S)$ is determined from the state–to–state calculations, with the requirement that it goes to zero when α_S approaches the $n_{S,v}^B(T_{v,S})$. The recombination rates are those reported in eq. 3.
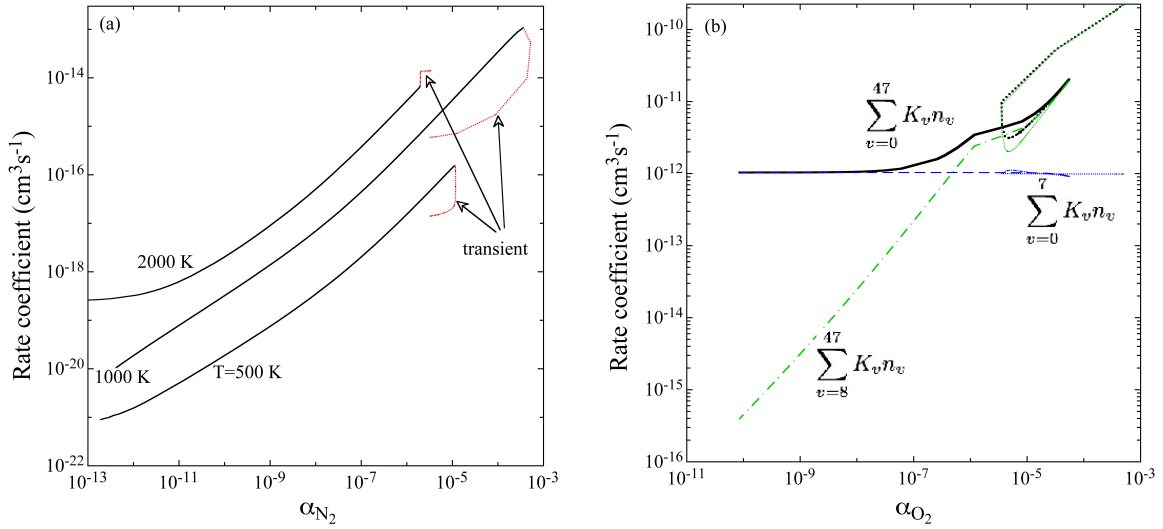
FIGURE 1. Rate coefficients of (a) $N_2 + O \rightleftharpoons NO + N$ and of (b) $O_2 + N \rightleftharpoons NO + O$ as a function of the distribution of the last vibrational level calculated with the STS model. The transient region have been evidenced with a dotted line. (a) The rates are reported for different gas temperature. (b) The different contribution to the rates have been put in evidence for T=1000 K.

Equation 4, together with eqs. 2,3 have been applied also to *NO* formation reactions. To determine the dependence of the rate coefficients on the population of the last vibrational level, time dependent calculations are performed starting from an initial vibrational temperature and gas composition fixing the pressure and the gas temperature to a value lower than the vibrational one in the simpler kinetic model: for N_2 and O_2 dissociation, the calculations where performed considering the pure gas. On the other hand, to determine the rate of the each Zel'dovich reactions, the N_2/N and O_2/O kinetics have been completed by adding only the process under study.

The TLD model is based on the hypothesis that the tail of the distribution reaches a quasi–steady state (see ref. [4, 5]): in the state–to–state calculation, we have a first phase, for time lower than t=10^{-8} s, where the distribution tail reaches a quasi–steady value. After that, the rates shows a regular dependence on the population of the last vibrational level of the molecule involved in the process. This result has been reported in fig. 1(a) for the $N_2 + O$ reaction, showing a loop corresponding to the transient phase. This behavior is very similar to N_2 dissociation [5]. However, the rate of $O_2 + N$, shows a completely different trend, being constant for low values of α_{O_2}. It must be noted that this process is exothermic, differently from $N_2 + O$, and therefore two different contributions must be considered: as can be observed in fig. 1(b) the total rate is the sum of a constant contribution coming from the low energy distribution ($v \leq 7$), and a growing contribution coming from the distribution tail ($v > 7$), strictly related to α_{O_2}. Also in this picture it can be noted the transient region, marked by dotted lines. Anyway, for both reactions, the rates can be expressed by eq. 4.

For the relaxation of the vibrational energy we use a strategy different from the multi–temperature model. The vibrational energy variation is given by the difference of gains (G) and losses (L)

$$\frac{dE_{v,S}}{dt} = G_{vT,S}(T, T_{v,S}) - L_{vT,S}(T, T_{v,S}) \tag{5}$$

due to vT calculated summing the state-to-state rates over a Boltzmann vibrational distribution multiplied by the variation of internal energy in the given transition.

In any case, the internal energy is related to the vibrational distributions considering the anharmonic energy levels of the diatomic species [8, 9]. It must be pointed out that in the TLD model the contribution of the vibrational energy to the chemical kinetics is very weak, except when the system approaches the chemical equilibrium.
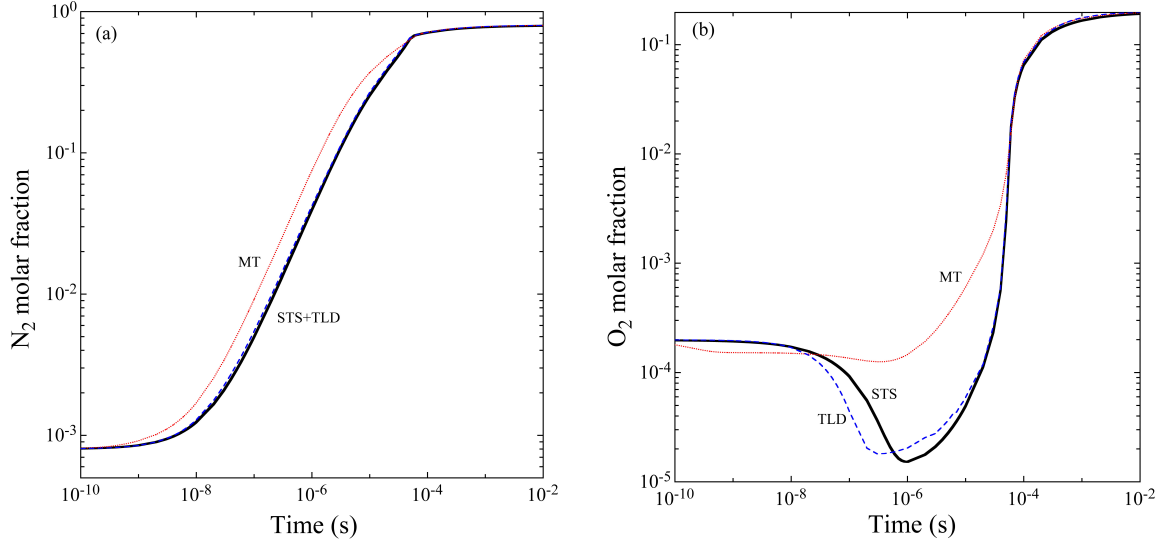
FIGURE 2. Time evolution of molar fractions of (a) N_2 and (b) O_2 for different kinetic models.

RESULTS

In this section we will compare the results obtained by the state–to–state (STS), multi–temperature (MT) and two–level distribution (TLD) models when relaxing an air mixture at atmospheric pressure to T=1000 K starting with the vibrational temperatures $T_{v,N_2}^0 = T_{v,O_2}^0 = 10000$ K and with the following initial molar fractions: $N_2 = 8\ 10^{-4}$, $N = 0.7992$, $O_2 = 2\ 10^{-4}$, $N = 0.1998$, $NO = 0$.

The TLD model determines molar fractions of N_2 and O_2 molecules (see fig. 2) in a very good agreement with STS in all the time interval while MT agrees with the other models only for t$> 10^{-5}$ s. In this case, the MT model underestimates the contribution of the distribution tails to the chemical processes. As a consequence, for N_2 this behavior results in lower dissociation rates, speeding up the recombination kinetics. The same behaviors are observed for O_2, where MT does not detect the decreasing of the molar fraction starting around t=10^{-8} s, because do not consider the contribution of the last level (see the rate in fig. 1(b)), and, as for nitrogen, anticipate the oxygen recombination with respect to STS.

Let's now examine the behaviors of the vibrational temperature (see fig. 3(a)) . The STS curve present a very high peak (up to $T = 90000$ K), due the atom recombination. This peak is not present in the macroscopic models, having neglected the contribution of recombination on the vibrational temperature. However, the MT model rapidly decreases, while the TLD reproduces quite accurately the vibrational temperature for t$> 10^{-4}$ s. It is not easy to include properly the contribution of recombination to the energy equation, because it is produced by two different steps: one is the direct recombination in low energy levels, one is the energy flux of highly excited molecules, produced by recombination and then depleted by vT. This last term needs further investigation to be determined, remembering that the high energy distribution is represented by the last vibrational level.

Let's consider the time evolution of the population of NO molecules (fig. 3(b)). This species is related to N_2 and O_2 vibrational distributions by the two Zel'dovich reactions. We can separate three regions in the time profile of NO. At short time, t$< 10^{-8}$ s, there is a transient phase, the system is adapting to reach the quasi–stationary conditions. In this phase neither TLD nor MT can reproduce the profile of STS. In the intermediate phase t$< 10^{-4}$ s, the TLD reproduces the STS results with a very good accuracy, while MT underestimates the value obtained with the other two models. For long times, t$> 10^{-4}$ s, both MT and TLD fail, even if this last gives a little better agreement. We must consider that the rate of the process $N_2 + O \rightleftharpoons NO + N$ used in TLD have been obtained neglecting the other Zel'dovich reaction ($O_2 + N \rightleftharpoons NO + O$) which shows dramatic effects in N_2 vibrational kinetics [2]. Therefore we determine the dependence of the rate coefficient of the first reaction on the population of the last N_2 vibrational level obtained from the complete calculation.

The rate presents a strange behavior, losing for a while the correlation with the last vibrational level. Therefore we
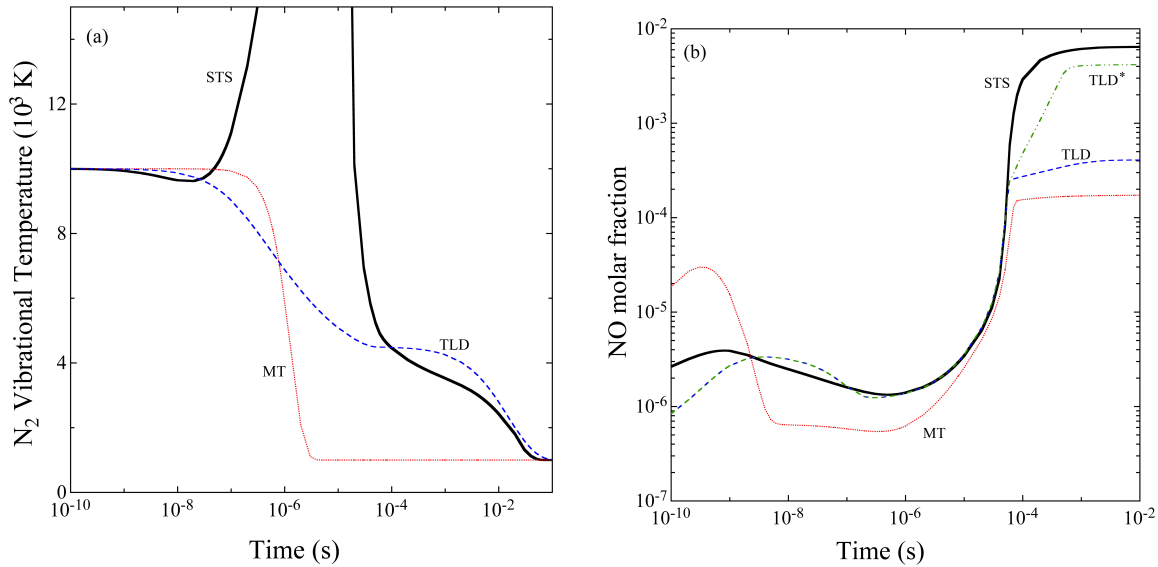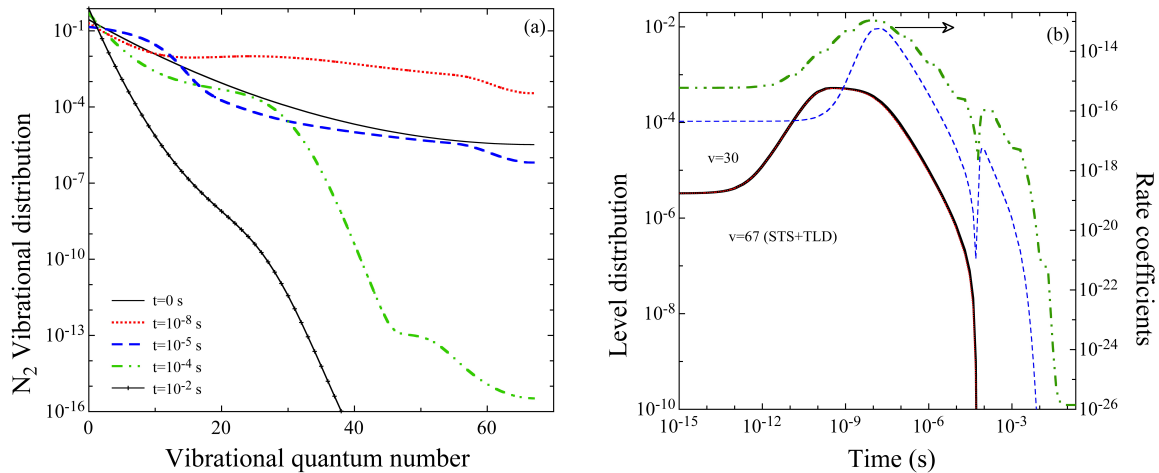
FIGURE 3. Time evolution of (a) N_2 vibrational temperature and (b) NO molar fractions for different models. The case $TLD^\star$ consider a dependence on the last vibrational level obtained in a complete STS calculation.

try to reproduce the trend of the rate using different fitting in different time intervals, obtaining in fig. 3(b) the curve marked as $TLD^\star$, which considerably improves the results calculated by the original TLD. This approach however does not follow the idea of the TLD; this is the symptom that the rate is not related to the last vibrational level, but to another quantity.

To investigate this behavior we have to study the evolution of the vibrational distribution (fig. 3(a)) and the time profile of the population of the last vibrational and one intermediate levels of N_2, compared to the rate of the first Zel'dovich reaction calculated in the complete STS model (fig. 3(b)). Up to t=10^{-10} s the last vibrational level is in a transient phase and the rate coefficient grows following its trend. However, in the quasi–steady state phase for the last vibrational level, the rate continues to grow, following the intermediate levels, also in the long time region, where both the population of the v=30 state and the rate coefficient present a maximum, while the last vibrational level shows a very low population.

We have already observed in ref. [2], that the second Zel'dovich reaction ($O_2 + N$) strongly affects the distribution of N_2, even if it is not directly involved in the process. This anomaly can be only explained in the framework of the state–to–state kinetics. As observed from fig. 4(a) the depletion of the tail of the N_2 distribution happens in the time interval between 10^{-5} s and 10^{-4} s, when the 90% of N atoms are already recombined and O_2 is forming. Now, the three body recombination is not the main process of N_2 formation, but has been overcome by two chain processes, $O_2 + N \rightarrow NO + O$ and $NO + N \rightarrow N_2 + O$, where the first one is very fast. Differently from the three body recombination, that produces mainly molecules in highly excited states, the chain reactions produce molecule in intermediate vibrational states. The overall effect is that the tails of the nitrogen vibrational distribution is not sustained by recombination, and is rapidly quenched by vT collisions, while intermediate vibrational states are growing, as observed in figs. 4(a,b), losing the correlation between the population of the last vibrational level and the related rate. The quenching of the distribution tail makes the global dissociation rate of N_2 to decrease, resulting in faster recombination kinetics.

A possible approach to include the effects of this phenomenon in TLD model could be to consider the rate coefficient as the sum of three different terms: a thermal (T, T_v) contribution, a term depending on the last vibrational level, and a term depending on the the product of N and NO molar fractions as the older approach described in ref. [4].

FIGURE 4. Time evolution of (a) N_2 vibrational distribution and (b) v=67 (*STS* and *TLD*), v=30 and the rate coefficient of the first Zel'dovich reaction (right axis) calculated in the complete *STS* model.

CONCLUSIONS

The Two-Level Distribution approach has been extended to the air mixture showing a good agreement with the state–to–state approach. A new model, based on state–to–state data, has been considered for the relaxation equation of the vibrational energy. The model should be completed by considering the contribution of chemical reactions to the energy equation. We have also shown that in some cases the last vibrational level is not sufficient to reproduce the rate coefficients, but other strategies should be explored. This model should also be included in fluid dynamic calculations, in particular in nozzle expansion, to extend its applicability to realistic applications.

The validity of the model in recombination regime has been proved in this paper, also for a complex mixture as air. The extension of the *TLD* model in dissociation regime will make this approach a general tool to simplify complex state–to–state kinetics in a proper way, such that the effects of non–equilibrium distributions can be included also in high dimensional (3D) fluid dynamic calculations.

ACKNOWLEDGEMENTS

REFERENCES

1. G. Colonna, M. Tuttafesta, M. Capitelli, and D. Giordano, *Journal of Thermophysics and Heat Transfer* **13**, 372–375 (1999), ISSN 0887-8722.
2. G. Colonna, M. Tuttafesta, M. Capitelli, and D. Giordano, *Journal of Thermophysics and Heat Transfer* **14**, 455–456 (2000), ISSN 0887-8722.
3. C. Park, *Journal of Thermophysics and Heat Transfer* **7**, 385–398 (1993).
4. G. Colonna, I. Armenise, D. Bruno, and M. Capitelli, *Journal of Thermophysics and Heat Transfer* **20**, 477–486 (2006).
5. G. Colonna, L. D. Pietanza, and M. Capitelli, *Journal of Thermophysics and Heat Transfer* **22**, 399–406 (2008).
6. D. Bose, and G. Candler, *Journal of Chemical Physics* **104**, 2825–2833 (1996), ISSN 0021-9606.
7. D. Bose, and G. Candler, *Journal of Chemical Physics* **107**, 6136–6145 (1997), ISSN 0021-9606.
8. F. Esposito, I. Armenise, and M. Capitelli, *Chemical Physics* **331**, 1–8 (2006).
9. F. Esposito, I. Armenise, G. Capitta, and M. Capitelli, *Chemical Physics* **351**, 91–98 (2008).
10. O. E. Krivonosova, and O. P. Shatalov, *Chemical Physics Reports C/C Of Khimicheskaia Fizika* **18**, 1621–1630 (1999).