

Energy-pooling collisions for K(4P)+Rb(5P) and Na(3P)+Rb(5P) heteronuclear systems

C. Gabbanini, S. Gozzini, G. Squadrito, M. Allegrini,* and L. Moi

Istituto di Fisica Atomica e Molecolare del Consiglio Nazionale delle Ricerche, Via del Giardino 7, 56100 Pisa, Italy

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The rate constants of the energy-pooling collisions in the Na-Rb and K-Rb vapor mixtures, resonantly excited by two cw dye lasers, have been measured relative to a known energy-pooling rate constant of a homonuclear reaction. To isolate the heteronuclear contribution in the fluorescence spectrum, a double-modulation technique has been adopted. The effective lifetimes of the excited levels that explicitly appear in the solution equation have been directly measured by using pulsed lasers. A discussion about the collision cross-section dependence on the energy defect involved in the energy-pooling collisions is reported.

I. INTRODUCTION

Resonant laser excitation of alkali-metal vapors, owing to the high oscillator strengths of their fundamental transitions, makes the study of processes involving excited atoms relatively easy.¹⁻⁴ The aim of these experiments is to measure the rate constants of the induced reactions and to compare them with the corresponding calculated parameters. Information on the atom-atom and atom-molecule intermediate-range interaction potentials is, in that way, obtained. The experiments, schematically very simple, present difficulties when a quantitative analysis is required because of self-trapping of the resonant photons and of the square dependence on the excited atomic density, which makes its absolute determination necessary. An incorrect evaluation of these two parameters may easily induce large errors, as it results from the early measurements which are spread over six orders of magnitude.⁵

The collisions between two excited alkali-metal atoms produce, at first, molecular ions, through the associative ionization (AI), and highly excited atoms, through the energy-pooling (EP) collisions. It is worthwhile to remind readers that the definition "energy pooling" was proposed by Bearman and Leventhal.⁶ They designated this term for all the processes involving two excited atoms, i.e., also those leading to associative ionization. During the last few years this definition has been instead associated only with the collisions in which there is double electronic energy transfer and we use "energy pooling" in this sense. If the vapor is optically very thick, secondary processes become important. They may lead to complete ionization of the vapor with laser power densities orders of magnitude lower than that required in the multiphoton ionization process.⁷ These effects have been, during the last few years, the subject of many experiments with alkali-metal atoms. Recently, new observations have been made with other atoms and EP collisions have been observed also in Sr vapor,⁸ while a new effect, the EP ionization, has been proposed for In and Tl atoms.⁹

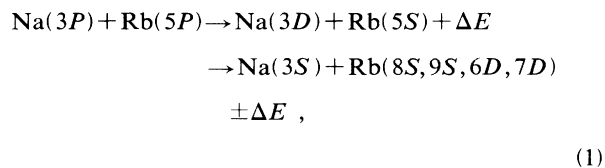
The aim of the present experiment is to study the EP collisions between different alkali-metal atoms under ex-

perimental conditions such that all the other processes are negligible.

EP collisions were observed for the first time by Allegrini *et al.*¹⁰ in sodium vapor. After that first experiment many others have been performed on alkali metals and the rate constant values of Na(3P)+Na(3P) and Rb(5P)+Rb(5P) reactions have been measured (see Table II). Recently, the study of EP collisions in heteronuclear systems has been proposed¹¹ and an experiment has been performed in the Na-K system leading to the first measurement of heteronuclear EP rate constants.¹² The Na-K mixture has also been studied in the presence of a buffer gas and direct evidence of three-body collisions has been obtained and an evaluation of the relative rate constant derived.¹³

In EP collisions two excited atoms produce one ground-state and one very-excited-state atom under the condition that the total internal energy is preserved in the limit of kT . Therefore the energy of the final excited level E_f must be $E_f = E_1 + E_2 + \pm \Delta E$, where E_1 and E_2 are the energies of the two laser-populated levels and $\Delta E \simeq kT$. This condition imposes severe limitations on the number of possible EP resonances for a given atom. In sodium, for example, only four excited levels can be efficiently populated by this mechanism. Many more EP resonance conditions (up to 60) can be found with heteronuclear systems by taking advantage of both the double level structure and the double independent laser excitation.¹¹

Here the results of new heteronuclear EP experiments, performed with Na-Rb and K-Rb mixtures, are reported. The atomic vapors are excited by using two cw dye lasers tuned to the fundamental transitions. The EP reactions studied are the following:

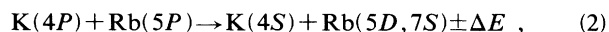


for sodium and rubidium, and these two others:

TABLE I. Characteristic parameters of the observed energy-pooling transitions.

Atom	Level	ΔE (cm^{-1})	Transition	λ (\AA)	γ	τ_{eff} (ns)
K	5P ^a	+1130	5P-4S	4045	0.26	
	6S ^a	-1591	6S-4P _{1/2,3/2}	6911-6940	0.59	
Rb	5D	+156	5D-5P _{1/2,3/2}	7619-7760	0.61	
	7S	-452	7S-5P _{1/2,3/2}	7280-7408	0.59	
	4F ^a	-910	4F-4D	13 446	0.98	
	7P ^a	-2011	7P-4D	11 744	0.15	
Resonance fluorescence						
K			4P _{3/2} -4S	7665		250±35
Rb			5P _{3/2} -5S	7801		300±45
Na	3D	+362	3D-3P _{1/2,3/2}	8183-8195	1	
Rb	8S	+488	8S-5P	6161	0.51	
	7D	-490	7D-5P	5726	0.7	
	6D	+846	6D-5P	6300	0.75	
	9S	-709	9S-5P	5655	0.47	
Resonance fluorescence						
Na			3P _{3/2} -3S	5890		200±30
Rb			5P _{3/2} -5S	7801		450±65

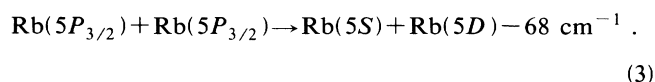
^aThese transitions have been observed only at higher temperature ($T=240^\circ\text{C}$) and are not taken in consideration for the corresponding K calculations.



for potassium and rubidium.

They give seven possible output channels and in Table I the energy defects ΔE , the emission wavelengths, and all the other useful parameters are reported. In Fig. 1 the simplified level schemes of the involved atoms are shown. The bold arrows represent the laser excitation, while the others the observed decay fluorescence lines. The dashed horizontal line gives the sum energy of the two laser-excited levels. The energy defect (for the high-lying levels) or excess (for the low-lying levels) is calculated with respect to this line.

The rate constants K_j of reactions (1) and (2) have been measured relative to $K_{5D}(\text{Rb})$, measured for the collision¹⁴



A double check with the known Na collision rate constants has been done for the Na-Rb system.

This indirect approach has been adopted because of the objective difficulty in measuring with sufficient precision the effective densities of the excited atoms and in deriving an absolute calibration of the detecting apparatus. In spite of a lower absolute accuracy of the K_j values (the error is of the order of 50%), this method gives, on the other hand, a bigger relative reliability because the line intensities and the effective lifetimes of the considered reactions are measured at the same time and under the

same conditions for all reactions.

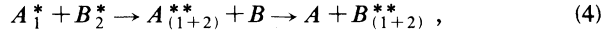
The measurement method is described in the following and the seven measured rate constants K_j are compared with all others previously obtained for alkali-metal atoms. A discussion on the K_j dependence on the energy defect ΔE is given in Sec. III.

II. MEASUREMENT PROCEDURE

The resonant laser excitation of optically thick alkali-metal vapors produces a very rich spectrum, resulting from atomic and molecular decay lines and bands.¹⁵ It is evident that the double resonant excitation makes this spectrum more crowded because of the separate contributions of the homonuclear and of the heteronuclear collisions. In order to measure the heteronuclear K_j it is therefore necessary to isolate the signals due to reactions (1) and (2) from all the others and, at the same time, to find the way to compare these signals with those of the reference reaction (3).

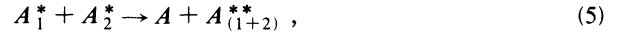
We have solved the problem by adopting an intermodulation technique which may have a very general applicability and that can be used every time heteronuclear processes take place. The two laser beams are modulated at two different frequencies ω_1 and ω_2 and the fluorescence is phase detected at ω_{1+2} . This procedure filters out the homonuclear part of the spectrum, which will have only one of the two modulation frequencies, and it transmits the heteronuclear contribution, which will have components modulated at the sum frequency. The

heteronuclear EP reactions can then be represented as



where the single asterisk and the double asterisk indicate the laser-excited and the collision-excited atoms, respectively; the subscript numbers denote the modulation frequency at which the levels are populated. To measure K_j

relative to the chosen homonuclear reaction, one of the two laser beams is split into two parts which are modulated at the two given frequencies. This permits a direct comparison between the signals, which are taken under the same exact conditions, and it eliminates the need for more elaborate calculations. The homonuclear reaction can then be written as



and it can be phase detected similarly to the heteronuclear one. The rate equations of the reactions (4) and (5), if secondary processes are neglected, are

$$\frac{d}{dt} N_j = -N_j \sum_{l \neq j} A_{jl} + K_j [A^*]_1 [B^*]_2, \quad (6)$$

$$\frac{d}{dt} \tilde{N}_i = -\tilde{N}_i \sum_{k \neq i} A_{ik} + \tilde{K}_i [A^*]_1 [A^*]_2,$$

where N_j and \tilde{N}_i are the densities of the EP populated levels, A_{mn} the Einstein coefficients, and $[A^*]$ and $[B^*]$ the densities of the laser-populated levels. K_1 is the reference rate constant. From Eq. (6) and under stationary conditions, we derive

$$K_j = \tilde{K}_i \left[\frac{\sum_l A_{jl}}{N_j \sum_{l \neq j} A_{jl}} \frac{[A^*]_2}{\tilde{N}_i \sum_{k \neq i} A_{ik}} [B^*]_2 \right]. \quad (7)$$

By introducing the experimental fluorescence line intensities

$$I_{mn} = \alpha_{mn} h \nu_{mn} A_{mn} N_{mn} V / 4\pi \quad (8)$$

and the branching ratios

$$\gamma_{mn} = \frac{A_{mn}}{\sum_{n \neq m} A_{mn}}, \quad (9)$$

where α_{mn} is a factor taking into account the efficiency of the detection apparatus, ν_{mn} is the transition frequency, and V the emission volume, Eq. (7) becomes

$$K_j = \tilde{K}_i \left[\frac{\alpha_{ik} \gamma_{ik} \nu_{ik} \tau_A}{\alpha_{jl} \gamma_{jl} \nu_{jl}} \frac{\tau_A}{\tau_B} \frac{\alpha_B \nu_B}{\alpha_A \nu_A} \frac{I_{jl}}{I_{ik}} \frac{I_A}{I_B} \right], \quad (10)$$

where τ_A and τ_B are the effective lifetimes of the two laser-excited levels and I_A and I_B the corresponding line intensities. From Eq. (10) K_j is known once the four involved line intensities and the effective lifetimes of the two laser-excited levels are measured.

III. EXPERIMENTAL APPARATUS AND RESULTS

The experimental apparatus is sketched in Fig. 2. An Ar^+ laser pumps two broadband cw dye lasers tuned to the two resonant frequencies of the considered heteronuclear system (see Fig. 1). With our apparatus it was not possible, at this stage, to laser excite the D_1 line of Rb.

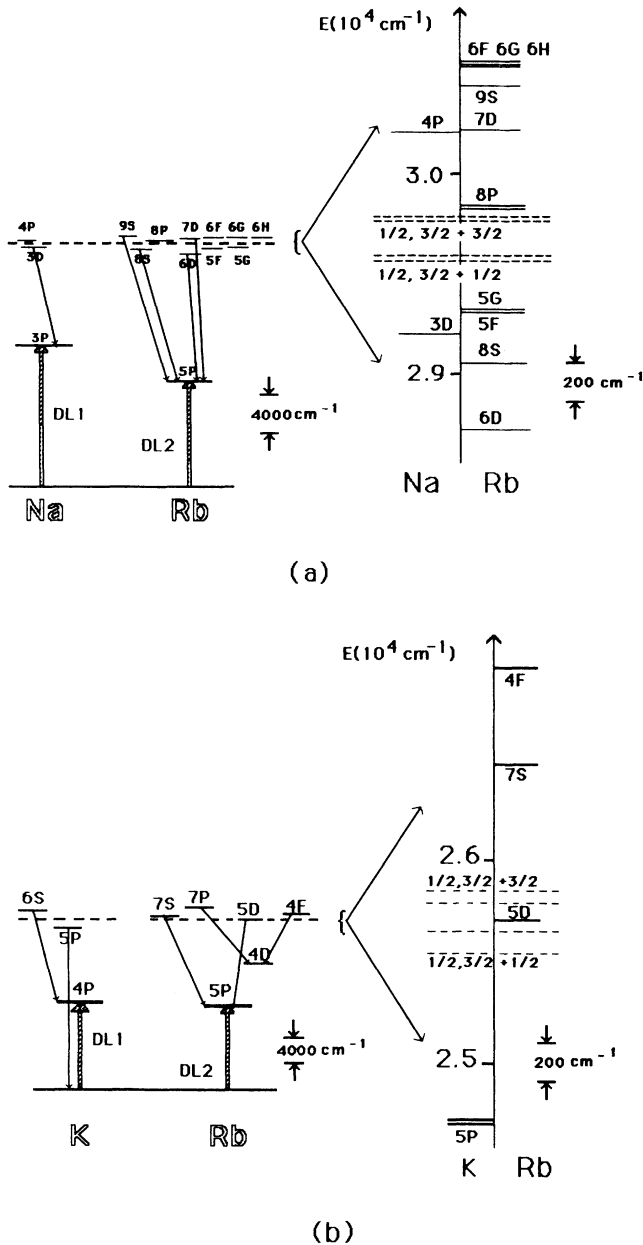


FIG. 1. Partial-energy level schemes of Na-Rb (a) and of K-Rb (b). The bold arrows represent the laser excitations and the down-pointing ones the observed transitions. DL1 and DL2 represent the resonant dye lasers. The horizontal dashed line gives the sum energy of the two laser-excited levels; the inset to the right shows, in an expanded scale, the positions of the EP populated levels.

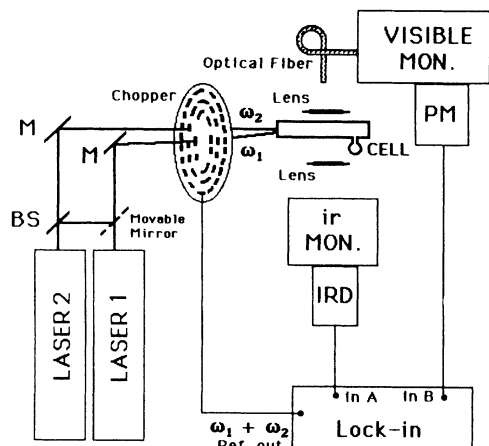


FIG. 2. Sketch of the experimental apparatus. The oven and the pulsed dye laser, used to measure the lifetimes of the laser-excited levels, are not shown. *M*, mirrors; *BS*, beam splitter; *MON*, monochromator; *PM*, photomultiplier; *IRD*, infrared detector.

Therefore all the measurements were made with D_2 excitation. It is, anyway, important to underline that, due to the high fine-structure-changing collision rate present at the working densities, there is always almost complete thermalization of the fine structure.

The two laser beams cross a mechanical chopper having three series of holes on it, arranged to give the three frequencies ω_1 , ω_2 , and $\omega_{1+2} = \omega_1 + \omega_2$. The lock-in amplifier is tuned to the sum frequency. The laser beam resonant with the Rb atoms is permanently split into two parts to allow, when both parts are sent into the cell, the

detection of the homonuclear collisions through the intermodulation technique and to have a direct comparison with the other atomic lines. The laser beams are superimposed at the entrance window of a capillary cell (internal diameter 2 mm), which contains in a sidearm the metal alloy, whose composition is made with quantities inversely proportional to the respective vapor densities of the two pure alkali metals taken at the working temperature (around $T = 200^\circ\text{C}$). This procedure gives reasonably comparable vapor pressures and it avoids the problems connected to secondary processes induced by too high vapor pressure of one of the two elements. Moreover, the excited volumes are about the same for the two lasers. In any case, a difference between these volumes does not affect the measurements if that of the more dense alkali-metal atoms is used as a reference, as in our case. The capillary geometry is useful to reduce the self-trapping and it gives favorable conditions to have a perfect superposition of the laser beams. The total density in the cells is of the order of 10^{13} atoms/cm³.

The fluorescence is collected at right angles by an optical fiber, which brings the light to the visible spectrum analyzer, and by a standard optical system for the ir monochromator. The fiber and the capillary geometry of the cell contribute to have a well-defined observation volume located immediately behind the cell entrance window. The two monochromators, one for the visible region and one for the near-infrared region, have been actually used in order to cover a wide region of the spectrum (from 300 nm to about $2\ \mu\text{m}$). They are coupled to a photomultiplier and a dry-ice-cooled PbS detector, respectively.

A pulsed dye laser (pulse width about 10 ns) is used to excite the alkali metals and to measure the effective life-

TABLE II. Available rate coefficients K and cross sections σ for energy-transfer collisions in alkali-metal systems.

System	Level	ΔE (cm ⁻¹)	T (°C)	K (10^{-10} cm ³ s ⁻¹)	σ (10^{-15} cm ²)	Ref.
Na-Na	5S	+716	210	3.8±1.3	4.0±1.4	16
	5S	+716	324	3.3±1.1	3.2±1.1	17
	4D	-602	210	6.0±2.1	6.4±2.1	16
	4D	-602	324	4.9±1.7	4.6±1.6	17
	4F	-642	250	1.2±0.6	1.2±0.6	18
Rb-Rb	5D	-69	180	30±12	64±26	14
	7S	-678	180	1.3±0.6	2.8±1.4	this work
Na-K	3D(Na)	+768	240	2.4±1.2	2.8±1.4	12
	5D(K)	-169	240	3.2±1.6	3.8±1.9	12
	7S(K)	-258	240	1.5±0.7	1.8±0.9	12
K-Rb	5D(Rb)	+156	220	36±18	58±29	this work
	7S(Rb)	-452	220	4.0±2.0	6.4±3.2	this work
Na-Rb	3D(Na)	+362	200	23±12	31±16	this work
	8S(Rb)	+488	200	13±7	17±9	this work
	7D(Rb)	-490	200	7±4	9.4±4.7	this work
	6D(Rb)	+846	200	6.4±3.2	8.5±4.3	this work
	9S(Rb)	-709	200	4.5±2.3	6±3	this work

times τ_{eff} of the laser-excited levels; the radiative lifetime is two orders of magnitude faster than the time between collisions at our working densities.

The measurement procedure is the following (1) the two lasers are switched on and a spectrum with the heteronuclear EP signals is recorded; (2) the sodium or potassium resonant laser is switched off and the split beam of the Rb resonant laser is sent inside the cell; a second spectrum is recorded in which the homonuclear EP collision lines are detected; (3) a pulsed laser is used to excite the atoms and to measure the decay time of the fundamental D lines; (4) the line intensities are corrected according to the instrumental response.

The measured K_j values are reported in Table II together with all the other reliable measured EP rate constants. The $K_{5D}(\text{Rb})$, similarly to the other K_j previously measured, has been doubled according to the analysis made by Bezuglov *et al.*¹⁹ They reconsider the AI rate constant definition as a function of the way the collisions are realized. They find that the K value obtained in the cell or in the beam for two identical particles has, with respect to the values obtained in double beams or with different particles, a factor 2 to be considered, a factor that has been previously neglected.

In Table II the $K_{7S}(\text{Rb})$ homonuclear rate constant is reported that has been measured by us with the intermodulation technique. This parameter has not been measured previously.

The total possible EP processes for the Na-Rb and K-Rb systems calculated by considering an energy defect or excess lower than $3kT$, are 15.¹¹ The rate constants effectively measured are instead 7, and precisely 5 for the Na-Rb system and 2 for the K-Rb one. The missing lines are those coming from the K($5P$), the Na($4P$), and the Rb($5F, 5G, 8P, 6F, 6G, 6H$) levels. For the P levels the uv fluorescence lines that have been observed are affected by self-absorption and attenuation by the Pyrex glass and lenses which make a reasonably precise evaluation of the effective level populations difficult. The corresponding ir lines are out of the detection range of our apparatus. It is worthwhile to mention here the fact that we did not have evidence in the spectrum of the level $8P$ of Rb, that owing to its very small energy defect, was supposed to be heavily populated. The level may decay to the ground state with a resonant wavelength equal to 3350 Å or to an intermediate S level with $\lambda=9550$ Å. Both the wavelengths are in regions of the spectrum where the apparatus has a very low sensitivity and that may be the cause of their absence. However, work is in progress to better understand this point. The other levels definitively decay with lines out of the spectral range covered by our apparatus and for that reason are missed.

The accuracy of the given rate constants is of the order of 50%. This error is due to the 35% error coming from the reference rate constant increased by that due to possible laser misalignment, intensity and frequency laser fluctuations, and uncertainty in the lifetime measurements.

In Fig. 3 all the available rate constants, measured for alkali metals, are plotted as a function of the energy defect or excess in a semilogarithmic scale. There are other K_j obtained for Na, but these are not considered here be-

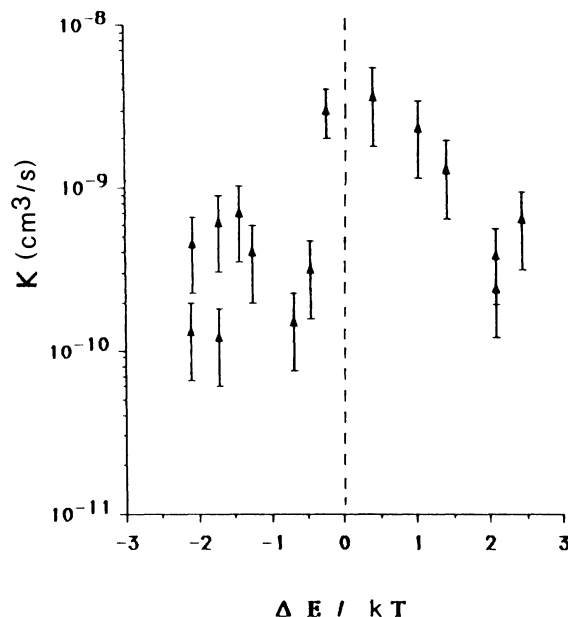


FIG. 3. Plot of the rate constant experimental values vs $\Delta E/kT$. $\Delta E/kT$ is positive when the EP populated level has an energy lower than the sum of the two laser-excited levels.

cause they are out, by many orders of magnitude, with respect to the values independently obtained by Allegrini *et al.*¹⁶ and by Gallagher *et al.*,¹⁷ which, instead, coincide in the limits of the given errors. Moreover, these last values have been confirmed by theoretical calculations.^{18,20}

Few considerations can be made by looking at this plot. If we consider the order of magnitude of the K values, the only fundamental parameter in determining them seems to be the energy defect ΔE , while there is a surprising lack of resonant contributions due to the particular structure of the considered system. This brings us to the conclusion that the particular shape of the intermolecular potentials changes only slightly the rate constant values because, probably, the density of the states that may intercross is always very high. This is particularly true in systems such as Na-Rb, while less restrictive for lighter systems such as Na-Na. Another consideration that can be derived from the plot is that the K values show two different behaviors as a function of ΔE . The rate constants corresponding to a reaction with positive ΔE can be fitted by the exponential decay function

$$K = (5.5 \pm 1.7) \exp \left[- \left(\frac{\Delta E}{kT} \right)^{1.4 \pm 0.2} \right] \times 10^{-9} \text{cm}^3/\text{s}.$$

For negative ΔE the dependence is steeper and the K values show a larger spread that does not permit us, joined with the reported errors, to do a significative fitting. This difference may be due to the presence of a potential barrier in the second case. This result, on the other hand, is different from what is observed in Sr atoms⁸ where no dependence on ΔE has been observed.

IV. CONCLUSIONS

The rate constants of seven heteronuclear EP collision processes have been reported and their values have been compared with that of the other alkali-metal atoms. The measured K_j do not manifest important deviations due to some particular interatomic potential interactions, but they show a dependence on the energy defect or excess. This dependence looks different depending on the sign of ΔE . A comparison with a theoretical evaluation of the same parameters would be desirable even if the task is not simple due to the complexity of the atomic interactions.

It would be, anyway, helpful to have a simple model able to predict the K dependence on a few parameters such as the energy defect, the principal quantum number, and others. This simpler approach seems to be justified after our measurements, which show a homogeneous behavior which, in first approximation, does not depend on the considered atomic system.

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*Permanent address: Dipartimento di Fisica, Università di Pisa, Piazza Torricelli 2, 56100 Pisa, Italy.

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