

## Single state $\text{NH}(X^3\Sigma^-, v=0, J, N)$ preparation for state-to-state studies

Jan Leo Rinnenthal<sup>a)</sup> and Karl-Heinz Gericke

*Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig,  
Hans-Sommer-Strasse 10, D-38106 Braunschweig, Germany*

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A new method is presented to examine state-to-state rotational energy transfer in ground state  $\text{NH}(X^3\Sigma^-, v=0, J, N)$ .  $\text{NH}(X^3\Sigma^-)$  is generated via state selective stimulated emission pumping using the strongly forbidden  $\text{NH}(a^1\Delta \rightarrow X^3\Sigma^-)$  intercombination transition around 794 nm after foregoing photodissociation of  $\text{HN}_3$  at a wavelength of 266 nm. Products are detected by laser induced fluorescence (LIF). Chemically relevant collision dynamics including spatial processes can be studied for the first time in  $v=0$  of the electronic ground state. State-to-state rate constants for inelastic collisions of  $\text{NH}(X^3\Sigma^-, v=0, J=3, N=3)$  with Ne are presented. © 1999 American Institute of Physics. [S0021-9606(99)01645-1]

Typical chemical processes occur in nature at temperatures around several hundred Kelvin where a broad range of rotational states is populated, but in terms of vibration most molecules are in the ground state. However, there is an essential lack of information on the dynamics of collisional energy transfer at these temperatures. No data for state-to-state energy transfer from higher  $J$  states than  $J=0,1$  within  $v=0$  of electronic ground state molecules are available. The reason for this large deficiency in our knowledge about the behavior of molecules in a typical chemical environment is a preparation problem of molecules in a single rotational state within the electronic and vibrational ground state. Until now, the direct measurement of rate constants for state-to-state rotational energy transfer in the electronic and vibrational ground state has only been possible for the lowest  $J$  state by decreasing the rotational temperature in a molecular beam. Such experiments, especially on the NH radical, were performed by Dagdigian *et al.*<sup>1</sup> Additionally a preparation of different  $\Lambda$ -levels and  $M_J$  substates can be achieved via electrostatic state selection in a hexapole electric field. ter Meulen and co-workers used this technique for single state selection in the OH radical.<sup>2</sup> State-to-state studies at higher rotations in the electronic ground state have only been performed for  $v>0$ <sup>3</sup> whereas experiments in  $v=0$  and at higher rotations have only been realized for electronically excited species, where one example is the NH molecule.<sup>4-6</sup> However, state selective laser preparation ( $J \gg 0$ ) has not been possible in the electronic and vibrational ground state.

There has been enormous experimental and theoretical interest over the last decades in the relaxation of systems by rotational energy transfer in collisions after they were initially displaced from equilibrium.<sup>7,8</sup> The knowledge of rate constants plays an important role in obtaining information about the potential energy surfaces of molecular systems and their ongoing dynamics. The development of state selective

laser preparation and detection techniques made it possible to determine state-to-state rate constants. Numerous experiments have been performed until now and a lot of experimental data is available for a multitude of closed and open shell molecules.

In order to answer the question of whether or how far existing data can be transferred to systems of species in the electronic and vibrational ground state, data on ground state molecules in higher  $J$  levels have to be accessible.

In the present work we present a technique of nearly unrestricted state selective preparation of ground state molecules applied to  $\text{NH}(X^3\Sigma^-, v=0, J, N)$ . This technique enables the study of state-to-state collision dynamics within  $v=0$  of the electronic ground state of a molecule for the first time. The technique is based on two steps. The first and crucial step is to generate a strong population inversion between the ground state of the molecule and a metastable excited state. In the second step (preparation) the ground state ( $v=0$ ) is state selectively populated by stimulated emission pumping. In order to perform subsequent state-to-state studies the ground state molecules can be detected as a function of collision numbers with reference to all quantum states in a further step by the use of laser induced fluorescence (LIF).

In the case of the NH radical a strong population inversion between the excited  $\text{NH}(a^1\Delta)$  state and the ground state  $\text{NH}(X^3\Sigma^-)$  is easily generated in the UV (ultraviolet) photolysis of hydrazoic acid ( $\text{HN}_3$ ).<sup>9-12</sup> In the present experiment, as first step  $\text{HN}_3$  is photolyzed by the fourth harmonic of a Nd:YAG laser at 266 nm where the population inversion is known to be 100%.<sup>11</sup> The pulse energy is 30 mJ and the beam is focused by a 500 mm lens. In the second step  $\text{NH}(X^3\Sigma^-, v=0, J, N)$  is prepared in a selected state by stimulating the strongly forbidden ( $\Delta S=1, \Delta L=2$ )  $\text{NH}(a^1\Delta \rightarrow X^3\Sigma^-)$  intercombination transition which has a radiative lifetime of  $\tau \approx 13 \text{ s}^{13}$  using intense laser light supplied by a Nd:YAG pumped dye laser at wavelengths around 794 nm and at a band width [full width at half maximum (FWHM)] of  $0.08 \text{ cm}^{-1}$ . The second step is performed 50 ns after the photolysis laser pulse to decrease the appear-

<sup>a)</sup> Author to whom correspondence should be addressed. Telephone: ++49 531 391-5346; Fax: ++49 531 391-5396. Electronic mail: j.rinnenthal@tu-bs.de

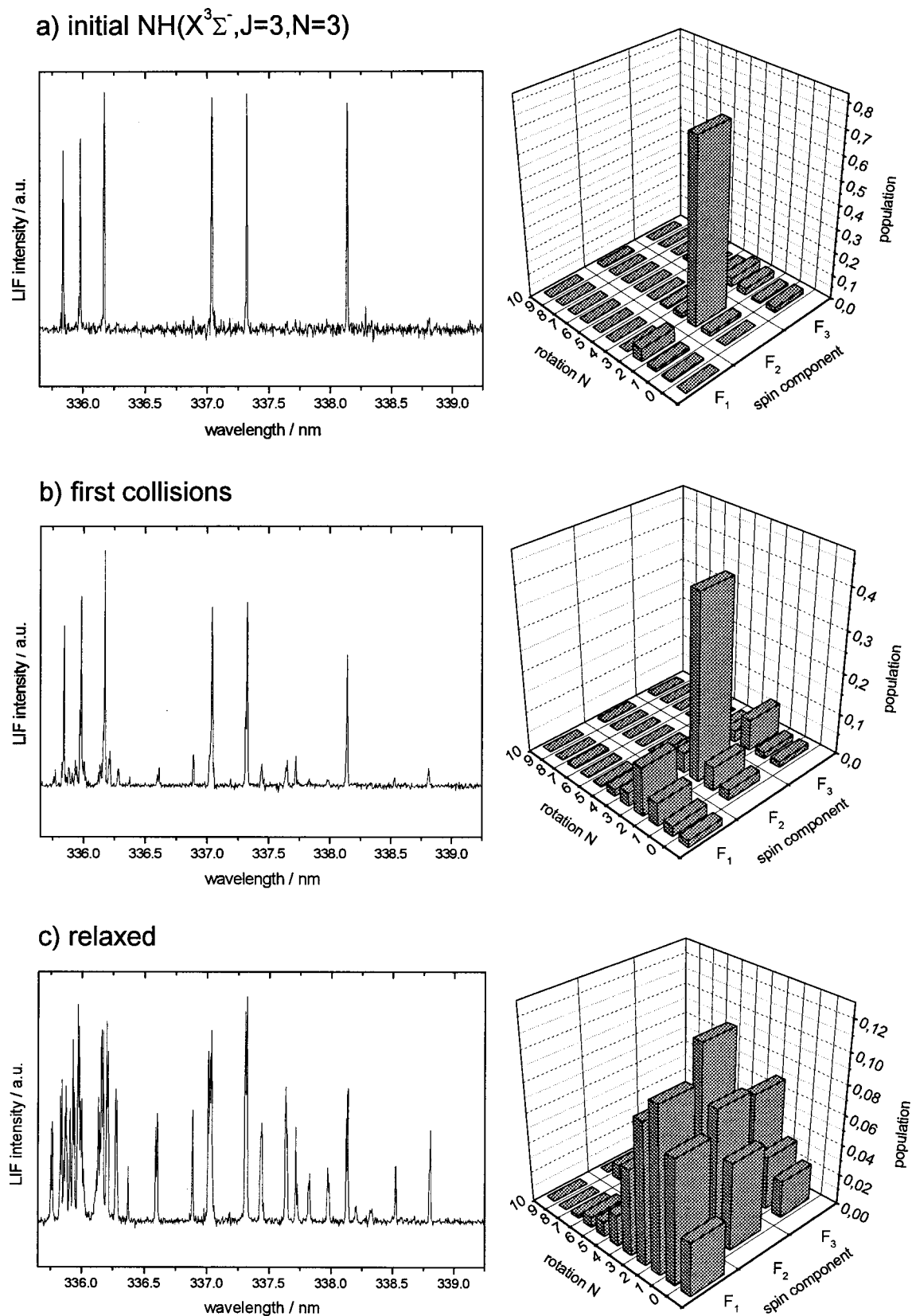


FIG. 1.  $\text{NH}(A^3\Pi, v=0 \leftarrow X^3\Sigma^-, v=0)$  LIF detection spectra of  $\text{NH}(X^3\Sigma^-)$  obtained by scanning the probe laser wavelength (left) and the corresponding quantum state populations (right). The initially prepared state is  $\text{NH}(X^3\Sigma^-, v=0, J=3, N=3)$ . The delays between the photolysis and the stimulated emission pulse and between the stimulated emission and the probe pulse are both set to 50 ns. The mixing ratio is  $\text{HN}_3:\text{Ne}=1:100$  and the total pressure in the observation chamber is (a) 200 Pa (nascent, all lines originate from the single  $F_2$  ( $J=3, N=3$ ) state), (b) 600 Pa [partly relaxed distribution essentially caused by primary collisions  $\text{NH}(J=3, N=3)$  with Ne], (c) 3200 Pa (almost relaxed to room temperature distribution).

TABLE I. Rotational transfer rate constants at  $T=300$  K in units of  $10^{-11}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ , for inelastic collisions of  $\text{NH}(X^3\Sigma^-, J=3, N=3)$  with Ne. The negative sign for  $F_2$ ,  $N=3$  indicates the decay of the initial level. Accuracy is  $0.08 \times 10^{-11}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ . Transitions which change the spin component are more effective than transitions which conserve the spin component. Spin component changing transitions have a propensity for conserving  $N$ . Within the  $F_2$  spin component  $\Delta J = \Delta N = \pm 1$  transitions are preferred.

$N$	$F_1$	$F_2$	$F_3$
0	0.24		
1	0.31	0.35	0.16
2	0.77	0.79	0.19
3	1.63	-7.68	1.06
4	0.48	0.70	0.31
5	0.21	0.22	0.08
6	0.05	0.00	0.00
7	0.06	0.00	0.00
8	0.04	0.00	0.00

ance of  $\text{NH}(X^3\Sigma^-)$  caused by electronical quenching of the  $\text{NH}(a^1\Delta)$  state.<sup>14-16</sup> In order to produce a photon flux that is sufficient to saturate the  $\text{NH}(a^1\Delta \rightarrow X^3\Sigma^-)$  intercombination transition the preparation beam (30–40 mJ/pulse) is focused by a 300 mm lens. With this preparation technique it is possible to completely selectively populate a wide range of ( $v=0, J, N$ ) states. Finally, the generated  $\text{NH}(X^3\Sigma^-, v=0, J, N)$  radicals are probed at different delay times via the  $\text{NH}(A^3\Pi \leftarrow X^3\Sigma^-)$  transition<sup>17-19</sup> applying the LIF technique under saturated conditions at a pulse energy of 1 to 2 mJ. The  $\text{NH}(A^3\Pi \leftarrow X^3\Sigma^-)$  spectrum contains all information about the quantum state population of  $\text{NH}(X^3\Sigma^-)$ . The delay time between the preparation and the probe pulse is varied to study the energy transfer from the initial ( $J, N$ ) state to the other ( $J', N'$ ) states. Alternatively, the pressure in the observation chamber can be varied in order to adjust a certain collision rate. The typical repetition rate in this experiment is 10 Hz. A photomultiplier monitors the fluorescence through  $f/1$  optics and an interference filter ( $330 \pm 30$  nm). The LIF signal is registered and averaged by a boxcar integrator.  $\text{HN}_3$  is generated by adding small amounts of phosphoric acid under vacuum conditions to sodium azide.<sup>20</sup> It is stored in a glass bulb at a maximum pressure of about  $10^3$  Pa and diluted with the desired collision partner X in a second glass bulb. The mixing ratio is chosen to be  $\text{HN}_3:\text{X}=1:100$  to assure that  $\text{NH}-\text{HN}_3$  collisions are rare in comparison to  $\text{NH}-\text{X}$  collisions being studied.

The  $a^1\Delta \rightarrow X^3\Sigma^-$  intercombination transition consists of nine branches denoted as  $^{\Delta N}\Delta J(J)$  where  $\Delta N$  represents the change of the nuclear rotation quantum number  $N$  and  $\Delta J$  represents the change of the total angular momentum  $J$ :  $^0P(J)$ ,  $^1P(J)$ ,  $^2P(J)$ ,  $^3P(J)$ ,  $^4P(J)$ ,  $^5P(J)$ ,  $^6P(J)$ ,  $^7P(J)$ , and  $^8P(J)$ .<sup>21</sup> In order to demonstrate that the technique is suitable to exclusively populate a single level for room temperature processes we used the  $^1P(3)$  line to generate  $\text{NH}(X^3\Sigma^-, v=0, J=3, N=3)$  as an example ( $E \approx 197$   $\text{cm}^{-1} \approx kT$ ). To quantify the exact state-to-state rate constants it is necessary to observe the  $\text{NH}(X^3\Sigma^-, v=0, J, N)$  population distribution for different collision numbers, i.e., different delay times between preparation and

probe pulse or different pressures. Figure 1 shows the observed LIF detection spectra (left) and the corresponding quantum state populations (right) for three different values of the total pressure, i.e., collision numbers, in the observation chamber. The first spectrum (a) at a total pressure of 200 Pa represents the detection of nascent  $\text{NH}(X^3\Sigma^-, v=0, J=3, N=3)$ . The second spectrum (b) at a total pressure of 600 Pa shows partially relaxed  $\text{NH}(X^3\Sigma^-, v=0)$  caused by primary collisions whereas the third spectrum (c) represents  $\text{NH}(X^3\Sigma^-, v=0)$  that is almost totally relaxed to room temperature distribution.

The time evolution of the populations of the rotational levels  $P_{J,N}(t)$  obeys a system of coupled differential equations (master equation) which can be written as

$$\frac{dP_{J,N}(t)}{dt} = N_c \left( \sum_{\substack{(J',N') \text{ max} \\ (J',N') \neq (J,N)}} P_{J',N'}(t) k^{(J,N) \leftarrow (J',N')} - P_{J,N}(t) \sum_{\substack{(J',N') \text{ max} \\ (J',N') \neq (J,N)}} k^{(J,N) \rightarrow (J',N')} \right), \quad (1)$$

for each single level ( $J, N$ ).  $N_c$  is the concentration of the collision partner (Ne),  $k^{(J,N) \leftarrow (J',N')}$  and  $k^{(J,N) \rightarrow (J',N')}$  are the rate constants. At time  $t_0$  when the dump laser prepares the initial level ( $J, N$ ), i.e.,  $P_{J,N}(t_0) = 1$  and  $P_{J',N'}(t_0) = 0$ , one obtains

$$\lim_{t \rightarrow t_0} \frac{dP_{J,N}(t)}{dt} = - \sum_{\substack{(J',N') \text{ max} \\ (J',N') \neq (J,N)}} \frac{dP_{J',N'}(t_0)}{dt} = - \sum_{\substack{(J',N') \text{ max} \\ (J',N') \neq (J,N)}} N_c k^{(J,N) \rightarrow (J',N')}. \quad (2)$$

The rate constants are then given by

$$k^{(J,N) \rightarrow (J',N')} = \frac{1}{N_c} \frac{dP_{J',N'}(t_0)}{dt}. \quad (3)$$

Equation (3) represents an approximation valid in the  $t \approx t_0$  regime where  $dP_{J',N'}(t)/dt$  is linear in  $t$ . Table I shows the rate constants for transitions originating from the  $\text{NH}(X^3\Sigma^-, J=3, N=3)$  level at a temperature of 300 K which were calculated by fitting the population data in the 0–50 ns region at a total pressure of 200–600 Pa. The data points used for the fit can be represented by a straight line which indicates that the effect of multiple collisions can be neglected. One recognizes that the rotational transitions within the  $F_2$  spin component occur for the most part to the neighboring levels ( $J=2, N=2$ ) and ( $J=4, N=4$ ). For transitions which change the spin component there is a propensity for conservation of the nuclear rotation quantum number,  $\Delta N=0$ . Finally, the total of the transitions which change the spin component are more effective than transitions which conserve the spin component.

The presented technique is also suitable to perform a detailed study of vectorial relaxation processes in the electronic and vibrational ground state. The high speed acquired in the dissociation process and the narrow bandwidth of the dump laser allows to select only those  $\text{NH}(a^1\Delta, v=0, J, N)$

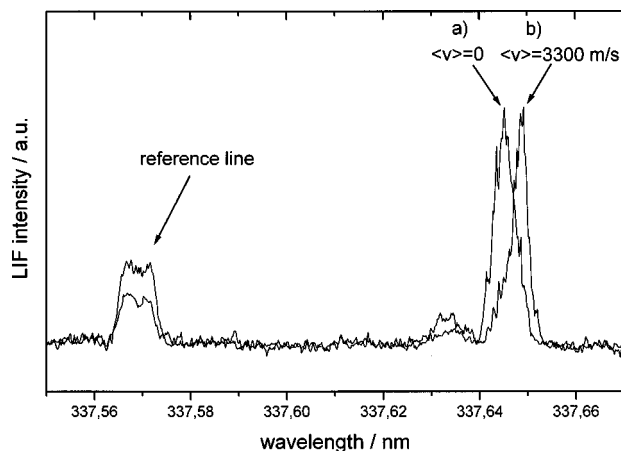


FIG. 2.  $Q_{12}(r)$  line in the  $\text{NH}(A^3\Pi \leftarrow X^3\Sigma^-)$  LIF detection spectrum of a  $\text{NH}(X^3\Sigma^-, v=0, J=4, N=4)$  beam prepared by using the  ${}^R R(4)$  line of the  $\text{NH}(a^1\Delta \rightarrow X^3\Sigma^-)$  intercombination transition for the stimulated emission (preparation). In case (a) only  $\text{NH}(a^1\Delta, v=0, J, N)$  radicals with a low velocity component in direction of the probe beam are selected for the stimulated emission [ ${}^R R(4)$  line peak] whereas in case (b) only those radicals are selected which exhibit a high velocity component in direction of the probe beam [side wing of the  ${}^R R(4)$  line]. The Doppler shift indicates a beam velocity of 3300 m/s which corresponds to the known velocity of the nascent  $\text{NH}(a^1\Delta)$  radicals in the photolysis of  $\text{HN}_3$  at 266 nm (Ref. 22). A reference line is used for calibration to assure that the observed line shifts between (a) and (b) is not caused by a wavelength shift of the dye laser emission. The delays between the photolysis and the stimulated emission pulse and between the stimulated emission and the probe pulse are set to 20 and 50 ns. The total pressure is  $p(\text{HN}_3) = 10$  Pa.

radicals for the stimulated emission to the  $\text{NH}(X^3\Sigma^-, v=0, J, N)$  state which exhibit a certain velocity component in the direction of the preparation beam. By this means it is possible to optically generate a molecular beam of  $\text{NH}(X^3\Sigma^-, v=0, J, N)$  radicals in a single  $(J, N)$  state. In that case the time delay between the photolysis and the preparation pulse has to be very small ( $< 25$  ns) in order to selectively transfer the translationally unrelaxed  $\text{NH}(a^1\Delta, v=0, J, N)$  fragments to the  $\text{NH}(X^3\Sigma^-, v=0, J, N)$  state under consideration. As an example, Fig. 2 shows the Doppler shift in the detection spectrum of a  $\text{NH}(X^3\Sigma^-, v=0, J=4, N=4)$  beam prepared that way. Then the spatial translational relaxation of these *oriented* molecules can be observed by monitoring the Doppler shifts and line profiles of the  $\text{NH}(A^3\Pi \leftarrow X^3\Sigma^-)$  detection spectrum of the initially populated NH state. Furthermore, the  $\langle \mathbf{v} \cdot \mathbf{J} \rangle$  correlation of  $\text{NH}(a^1\Delta, v=0, J)$  for higher  $J$  levels in the photolysis of  $\text{HN}_3$  at 266 nm is positive,<sup>22,23</sup> i.e., the vectors for translational and rotational motion are aligned parallel to each other. Thus, an observation of relaxation effects concerning the alignment of the  $\mathbf{J}$  vector in the prepared  $\text{NH}(X^3\Sigma^-, v=0, J, N)$  state by the intensity ratio between the  $P$  and  $Q$  lines in the detection LIF spectrum at different collision numbers is also feasible.

A preparation technique is presented that can be used to selectively populate single rotational levels of molecules in their electronic and vibrational ground state allowing de-

tailed studies on chemically relevant collision dynamics in the thermal energy regime which has been inaccessible for state-to-state studies so far. The technique is applicable to a wide range of molecules provided a population inversion can be achieved. Spatial relaxation processes in rotationally inelastic collisions can be studied if a narrow band laser is used to prepare an oriented sample of single quantum state molecules. Molecule-specific vector correlations, e.g., the  $\langle \mathbf{v} \cdot \mathbf{J} \rangle$  correlation allows to prepare a  $M_J$  sub-states distribution. Furthermore, it is understood that also vibrational excited states, like  $\text{NH}(X^3\Sigma^-, v=1, J, N)$ , can be prepared state selectively. This allows a direct comparison of the rate constants for  $v=0$  and  $v>0$  states.

Series of measurements for all preparable  $\text{NH}(X^3\Sigma^-, v=0, J, N)$  levels are in progress. An extensive application of this technique and a detailed study of the relaxation phenomena in ground state  $\text{NH}(X^3\Sigma^-, v=0, J, N)$  including a study of multiple collisions by solving the master equation [Eq. (1)] will be given in a forthcoming paper.

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