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# Resonance-like phenomena in activated dissociative adsorption: $\text{N}_2^+$ on Ni(100) and Ni(111)

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Atomic nitrogen adsorption on Ni(100) and Ni(111) surfaces was studied by using very low energy (1–20 eV)  $\text{N}_2^+$  and  $\text{N}^+$  ion beams. The amount of adsorbed nitrogen was measured by Auger electron spectroscopy as a function of the incident energy of the ions. The adsorption rate for  $\text{N}^+$  is almost a constant, whereas the dissociative-adsorption rate for  $\text{N}_2^+$  is strongly energy dependent. In the latter case, there exist two channels; one has a low apparent activation barrier of about 1 eV and the other of about 5 eV. A resonance-like feature in the low-activation-barrier reaction was observed at the incident energy of 2–3 eV on Ni(100) and ~4 eV on Ni(111). The adsorption rate is independent of the angle of incidence. The resonance-like feature is explained by a model which assumes that electronically excited molecules produced by resonance neutralization of the incident ions are dissociatively adsorbed over the low activation barrier and the excited molecules are deexcited on the surface at higher incident energies.

## I. INTRODUCTION

The dynamics of atoms and molecules on solid surfaces is important in understanding complex chemical reactions on heterogeneous catalysts. Supersonic molecular beams of thermal energy (below 1 eV) have been successfully used to gain insight into the microscopic mechanisms of direct inelastic scattering,<sup>1,2</sup> trapping desorption,<sup>2,3</sup> and velocity-dependent sticking. In the hyperthermal energy range, however, few experimental works have been carried out, because the highest energy attainable by the seeded supersonic molecular beam is only about 2 eV for light diatomic molecules. In addition to these experimental difficulties, quantitative theoretical description of the interaction between molecules and surfaces is far from being successful in the present state.

The energy range from 1 to 10 eV will provide interesting chemical processes associated with a nonadiabatic process such as electronic excitation, vibrational excitation, dissociation followed by the chemical-bond formation, and trapping in a shallow attractive potential well on surface. The ion beam can easily be accelerated into this energy range. However, very-low-energy ion beams have been scarcely employed to study dynamical processes on surfaces. In a usual ion beam apparatus, the beam divergence and the space charge effect make it difficult to get sufficient ion current onto the target below the beam energy of 100 eV. Even if collimated bright ion beams are obtained, it is not easy to detect scattered ions, because ion survival probability falls close to zero in this low energy region. Only hyperthermal alkali metal scattering<sup>4,5</sup> and rainbow scattering of alkali metal ions<sup>6,7</sup> have been carried out. Therefore, ion beam scattering using incident energies higher than 200 eV has been developed as an analytical tool to elucidate the elemental composition of surfaces or the surface structure; this method is called ISS (ion scattering spectroscopy).<sup>8</sup> This ion beam energy is too high to be applied to the study of molecular dynamics except for the study of ion neutralization.

We have studied a dynamical process of dissociative adsorption by using  $\text{N}_2^+$  and  $\text{N}^+$  ion beams of the incident kinetic energies from 1 to 20 eV in the present work. Dissociative adsorption is one of the fundamental chemical processes on surfaces. The amount of nitrogen adsorbed dissociatively on targets of Ni(100) and Ni(111) was measured by using Auger electron spectroscopy (AES). The dissociation process of  $\text{N}_2$  on metal surfaces is important, because it is an elementary step in ammonia synthesis on catalyst. It is known that thermal  $\text{N}_2$  molecules are not dissociatively chemisorbed on a Ni surface at room temperature and that  $\text{N}_2$  is molecularly adsorbed at low temperatures.<sup>9</sup> The potential barrier for the dissociative adsorption breaking the triple bond of a  $\text{N}_2$  molecule on a Ni surface amounts to about 1.6 eV,<sup>10</sup> which is too high to be surmounted by thermal energy. On the other hand, it has been shown that the chemisorption takes place when accelerated ions impinge onto the Ni surface.<sup>11</sup>

Activated dissociative adsorption has recently attracted much attention of experimentalists and a fair number of studies have been carried out by using the molecular-beam technique. The increase of the translational energy of incident molecules is efficient in breaking the chemical bond. For most of the projectile molecules such as  $\text{H}_2$ ,<sup>12–14</sup>  $\text{CH}_4$ ,<sup>15–18</sup>  $\text{O}_2$ ,<sup>19,20</sup> and  $\text{CO}_2$ ,<sup>21</sup> the sticking probability is given by the normal energy of the incident molecule (normal energy scaling). The only one exception has been known for  $\text{N}_2$  adsorption on W(110), where the sticking probability scales with the total energy.<sup>22</sup> However, the role of the translational energy in the microscopic mechanism is not known at all. The energy transfer is directly linked with the theoretical question on how the translational energy is converted to vibrational<sup>23</sup> or rotational<sup>24</sup> energy and which of the vibration and rotation is more effective in dissociating molecules on surfaces.

In the present result, a resonance-like feature was observed for the first time in the dissociative-adsorption rate as

a function of the incident energy. This very-low-energy ion beam technique applied to the reaction on surfaces<sup>25,26</sup> is a unique method to study the reaction mechanism in a wide incident-energy region.

## II. EXPERIMENT

The present experimental apparatus is described briefly elsewhere.<sup>27</sup> Figure 1 shows the schematic representation of the ion beam source. A bright ion source of the Menzinger type used here has a narrow energy spread of  $<0.2$  eV.<sup>28</sup> In order to obtain a high-intensity beam, a mass-selecting magnet for the incident beam was installed in an ultrahigh-vacuum chamber and an efficient decelerating-lens system was used to obtain a well-collimated beam. The ion current of  $N_2^+$  was 15–38 nA over the incident energy range from 1 to 20 eV, whereas the  $N^+$  beam current was 5–18 nA above 3 eV with increased  $N_2$  gas pressure in a BN (boron nitride) cell. The intensity of the  $N^+$  beam could not sufficiently be obtained for the measurement below 2 eV. Though the base pressure in the collision chamber was  $7 \times 10^{-11}$  Torr, the operating pressure in the chamber rose to  $1\text{--}2 \times 10^{-9}$  and  $3\text{--}6 \times 10^{-9}$  Torr for the duration of exposure to the  $N_2^+$  and  $N^+$  beams, respectively. A pressure gauge was switched off during ion beam exposure to avoid generating background ions. About 80% of the incident ion beam intensity was confined in a circular area of 4 mm in diameter on the sample surface irrespective of the incident energy. The beam profile was measured by a probing rod placed next to the sample. The current density in this round area was found to be uniform with a deviation of  $\pm 15\%$ .

The beam exposure time was set at a constant beam exposure of  $6 \times 10^{-7}$  A min, which corresponds to  $1 \times 10^{15}$  ions/cm<sup>2</sup> in the area. The ion current was measured by a Faraday cup aligned using a laser beam. The  $(1 \times 1)$  structure for both Ni(100) and Ni(111) was observed by low-energy electron diffraction (LEED) and did not change at all in the range of the above exposure. However, the LEED pattern showed diffuse  $c(2 \times 2)$  and  $p(2 \times 2)$ -like structures for Ni(100) and Ni(111), respectively, for higher beam exposures. From these results and the AES data, nitrogen coverage is estimated to be  $<0.1$  monolayer in the present ex-

periment and thus the sticking probability for incident ions is expected to be constant. Hence, the amount of adsorbed nitrogen, which was determined from the ratio of the AES peak-to-peak intensity of N at 380 eV to that of Ni at 716 eV, is proportional to the adsorption rate of atomic nitrogen. The surface temperature was 300 K.

The following processes were performed for each observation. Adsorbed N atoms were removed by  $Ar^+$  ion sputtering of 500 eV during 20 min and 2 min annealing at 970 K. A clear  $(1 \times 1)$  structure was checked by LEED observation and the surface cleanliness was monitored by the AES measurement. The surface concentration of C, O, and S was  $<1\%$  of one monolayer. The beam spot size was observed and the ion current was measured. Next, the ion beam impinged on the center of the Ni surface for the time of the constant ion exposure  $6 \times 10^{-7}$  A min. Finally the amount of nitrogen adsorbed on the surface was measured at more than 6–10 points in the round area of 4 mm in diameter and the mean value of these observed intensities was plotted in Figs. 2 and 3.

## III. RESULTS

Figures 2 and 3 show the amount of N atoms adsorbed on Ni(100) and Ni(111), respectively, after the constant beam exposure as a function of the incident kinetic energy. The intensity for  $N^+$  incidence in these figures is twice the observed intensity, since two atoms contribute to adsorption for each incident  $N_2^+$  ion and one atom for each  $N^+$  ion. The angle of incidence  $\theta_i$  was  $0^\circ$  (normal incidence). Error bars accompanying these data points were estimated from 3–5 independent observations for  $N_2^+$  incidence and two observations for  $N^+$  incidence, and indicate about 90% confidence limits for the relative intensities. It is estimated from coverage and exposure that an AES intensity ratio of 1.0 shown in the ordinate of Figs. 2 and 3 corresponds to a sticking probability of about 0.15.

The nitrogen adsorption rate for  $N^+$  incidence is nearly

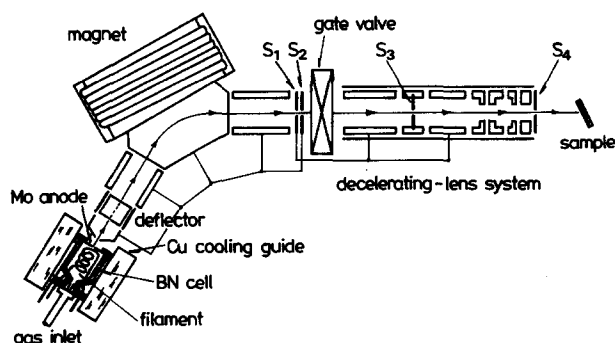


FIG. 1. Schematic representation of the ion source, mass-selecting magnet, and decelerating lens system. Incident energy of the ion beam is determined by the potential difference between the Mo anode and the target sample.

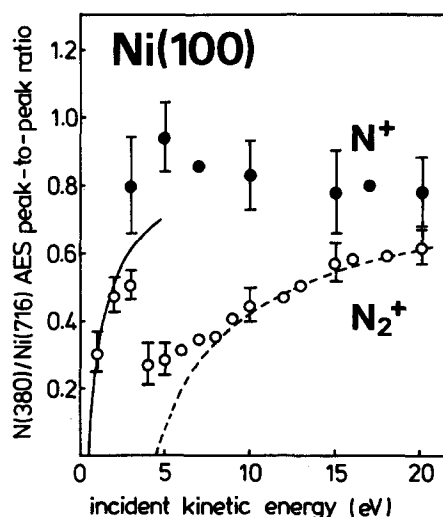


FIG. 2. Nitrogen adsorption rate on Ni(100) as a function of the incident energy for  $N_2^+$  (open circles) and  $N^+$  (solid circles) ions at normal incidence.  $\sigma_1(E)$  and  $\sigma_2(E)$  are shown as solid and dotted lines, respectively.

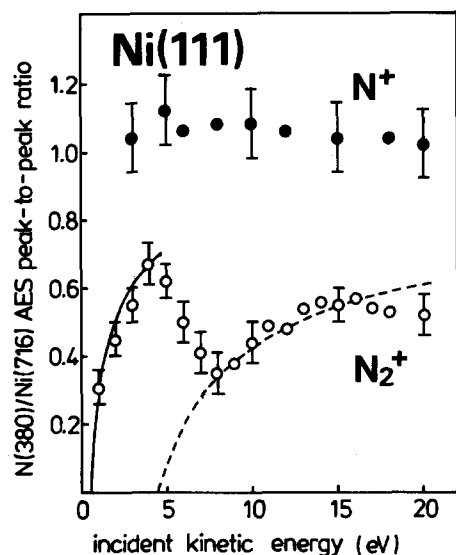


FIG. 3. Nitrogen adsorption rate on Ni(111) as a function of the incident energy for  $N_2^+$  (open circles) and  $N^+$  (solid circles) ions at normal incidence.  $\sigma_1(E)$  and  $\sigma_2(E)$  are shown as solid and dotted lines, respectively.

constant or slightly decreases with increasing energy on both surfaces. This observation is similar to the pioneering work of  $N^+$  adsorption on polycrystalline Mo surface.<sup>25</sup> This result shows that an  $N^+$  ion of an atomic form can be adsorbed as it is and that the sticking probability of atomic nitrogen on the surface is independent of the incident energy.

In contrast, the dissociative adsorption rate of  $N_2^+$  ion shows a strong energy dependence and a resonance-like feature on both surfaces. In the case of Ni(111), the adsorption rate increases rapidly with increasing energy, reaches a maximum at 4 eV, decreases abruptly, and again increases gradually through a minimum point at 8 eV, as shown in Fig. 3. The result for Ni(100) is similar to that in Ni(111), but the incident energies corresponding to the maximum and the minimum rate are shifted to lower values, as shown in Fig. 2. This is the first observation of a resonance-like feature in the dissociative-adsorption rate on the surface. These results are clearly different from the observation in a similar experiment of  $N_2^+$  impinging on Ni(111) by Shamir *et al.*<sup>26</sup> The AES intensity of their result exhibits a plateau in the region from 2 to 6 eV. This discrepancy probably arises from the different amount of ion exposure or the different surface cleanliness. Incidentally, their result of  $N_2^+$  incidence on the polycrystalline Cu surface appears to show a maximum intensity at 4 eV,<sup>26</sup> which is similar to the present result, though they ignored it.

We further examined the  $\theta_i$  dependence of the adsorption probability at a few incident energies. Since the number of incoming ions per unit surface area is proportional to  $\cos \theta_i$ , the intensity divided by  $\cos \theta_i$  is shown in Fig. 4. The adsorption rate of  $N_2^+$  is nearly constant with respect to the angle of incidence. It is not easy to judge clearly whether the adsorption rate of  $N_2^+$  on Ni obeys the normal or total energy scaling from Figs. 2–4. The adsorption rate does not change sufficiently with incident energy and is not a mono-

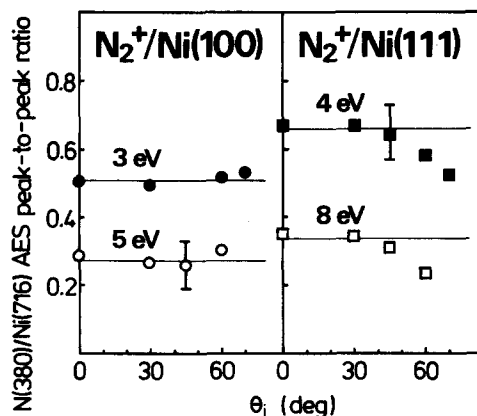


FIG. 4. Incidence angle dependence of nitrogen sticking probability for  $N_2^+$  incidence on Ni(100) and Ni(111).  $\theta_i$  is measured from the surface normal.

tonic function over the energy region where the measurements were made. However, if we apply criterion to the present results that the adsorption rate is constant with respect to the incidence angle, the dissociative adsorption rate of  $N_2^+$  on Ni satisfies the total energy scaling, and not the normal energy scaling.

There are at least two channels in the incident-energy dependence of the dissociative-adsorption rate of  $N_2^+$  on Ni surface (Figs. 2 and 3): Channel 1 corresponds to the resonance-like feature in a lower-incident energy part of 1–5 eV in Ni(100) and 1–8 eV in Ni(111), and channel 2 corresponds to the gradual increase of the adsorption rate in a higher-energy part. A typical simple model shows the energy dependence of the adsorption cross section for channel  $i$  as,<sup>29</sup>

$$\begin{aligned}\sigma_i(E) &= \bar{\sigma}(1 - E_{ai}/E), \quad \text{for } E > E_{ai}, \\ \sigma_i(E) &= 0, \quad \text{for } E < E_{ai},\end{aligned}\quad (1)$$

where  $E_{ai}$  is an apparent activation barrier and  $E$  is the total kinetic energy of the molecule upon impact, i.e., the sum of the incident energy and the kinetic energy gain of 0.5 eV due to the image charge before resonance neutralization. This relation was applied to the increasing region of the channels 1 and 2, and the parameter values of  $E_{a1} = 1$  eV and  $E_{a2} = 5$  eV fit to the experimental data well for both Ni(100) and Ni(111). These  $E_{ai}$  values include the uncertainty of  $\pm 0.5$  eV. The curves of  $\sigma_1(E)$  and  $\sigma_2(E)$  are shown as solid and broken lines, respectively, in Figs. 2 and 3.

The comparison between Figs. 2 and 3 suggests that the difference of the surface plane is reflected in the region of the abrupt decrease. Then, the critical energy of channel 1 is structure sensitive, at which the adsorption rate decreases abruptly. Channel 1 is characterized by a low activation barrier, which is independent of the kind of the surface plane. This channel is open at even the lowest energies of 1 eV but is not accessible at energies higher than the critical energy.

#### IV. DISCUSSION

There exist many electronically excited states, into which  $N_2^+$  is transferred after accepting a valence electron of Ni. Since antibonding orbitals accepting the valence electron

(especially  $\pi^*$  orbitals) are spatially extended, almost 100% of incoming  $N_2^+$  ions are neutralized into  $N_2^*$  by resonance neutralization at a point 6–10 Å away from the surface. The most probable states are  $a^1\Pi_g$  and  $B^3\Pi_g$ .<sup>30</sup> The kinetic energy gain  $\Delta E$  due to the image charge effect before the resonance neutralization is only about 0.5 eV. Vibrational energy  $E_v$  of the incident beam is difficult to estimate but is thought to be < 2 eV. When the incident energy  $E_i$  of ions is 1 eV, the total energy,  $E_i + \Delta E + E_v$ , is smaller than 3.5 eV. Even if we suppose that all of this energy is used to break the  $N_2$  bond, it does not exceed the dissociation energies for  $a^1\Pi_g$  (5.97 eV) and  $B^3\Pi_g$  (4.76 eV).<sup>31</sup> The dissociation energies of  $N_2^+$  ( $X^2\Sigma_g^+$ ) and ground state  $N_2$  ( $X^1\Sigma_g^+$ ) are larger than these values; e.g., 9.76 and 8.72 eV, respectively.<sup>31</sup> The tunneling effect<sup>12</sup> is negligible in the case of  $N_2$  dissociation. Though the dissociation energy of the  $C^3\Pi_u$  state is as small as 2.29 eV, this state lies at 0.7–0.8 eV above the Ni Fermi level and molecules excited to this state cannot be produced by resonance neutralization.

In the above arguments, the dissociation energy of a free molecule is used and the existence of Ni surface is ignored. When  $N_2$  is dissociated on the surface and a Ni–N bond is formed, the energy level of two dissociated N atoms is lowered by 11.5 eV due to the bond formation in comparison with that of free atoms.<sup>10</sup> Hence, the activation barrier for dissociation leading to adsorption is expected to be lowered. A schematic energy diagram of our model for the explanation of the present experimental results is shown in Fig. 5. The activation barrier for the dissociative adsorption is given by the sum of the apparent activation barrier fitted by Eq. (1) for channel 1,  $E_{a1} = 1$  eV, and the vibrational energy  $E_v$ . The dissociative adsorption from  $N_2^*$  produced by the resonance neutralization can explain a low activation barrier observed in channel 1.

The low activation barrier may be interpreted by other models. Willerding *et al.*<sup>30</sup> suggested that  $a^1\Pi_g$  can be pre-dissociated to the  $^5\Sigma_g^+$  state, if primary ions are sufficiently ( $v = 6$ ) vibrationally excited. However, since the transition between these states is forbidden in a free molecule, the pre-

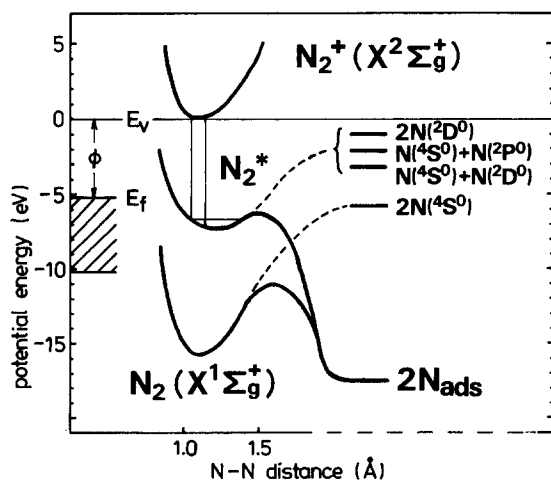


FIG. 5. Schematic energy diagram of the reaction mechanism for the interpretation of the present experimental results.

dissociation probability is considered to be by far lower than the dissociative adsorption rate observed in the present experiment.

Next we will consider the origin of the abrupt decrease of the adsorption rate in channel 1. As the incident energy increases, the closest approaching point becomes closer to the surface. Approaching a region where the orbital of a  $\sigma$  hole in  $N_2^*$  interacts with the Ni  $d$ -band orbital,  $N_2^*$  is deexcited into the ground state  $X^1\Sigma_g^+$  by Auger deexcitation. If  $N_2^*$  is deexcited into the ground state without leading to the dissociative adsorption from the electronically excited state, the adsorption rate abruptly decreases due to a larger dissociation energy of  $X^1\Sigma_g^+$ . The partially occupied antibonding orbital resulting from the resonance neutralization is spatially extended in a broader region than the  $\sigma$  hole orbital.<sup>32</sup> Therefore, the interaction region where the dissociative adsorption takes place in channel 1 is extended away from the surface in comparison with the case of Auger deexcitation. If excited molecules pass through this extended region over a time enough to cause molecular deformation, the molecules will proceed to dissociative adsorption before deexcitation. The closest-approach distance  $r_0$  between a molecule and a Ni atom in the collision can be estimated by the Born–Mayer potential.<sup>33</sup> If we use parameters for Si (mass number 28) atom instead of  $N_2$  and impact parameter is taken as zero,  $r_0 = 2.5$  Å at  $E = 1$  eV, and  $r_0 = 2.0$  Å at  $E = 5$  eV, and  $r_0$  decreases with increasing energy. Since it is generally accepted that the region where Auger neutralization takes place is < 2 Å away from the surface and this distance is equivalent for Auger deexcitation, the explanation described above is reasonable for the abrupt decrease of the adsorption rate above the critical incident energy.

The real surface is two dimensional with corrugation depending on the surface plane. The impact point on the surface as well as the orientation of the incoming molecule will considerably affect the effective distance  $r_0$  and then the deexcitation probability. Although full calculations taking such factors into consideration are necessary to quantitatively account for the result, the difference of the average deexcitation probability depending on the surface structure is considered to be reflected in the different critical energies between Ni(100) and Ni(111), as shown in Figs. 2 and 3.

Above the critical energy, almost all of  $N_2^*$  molecules are deexcited. The dissociative adsorption rate of channel 2 obeys the same relation of Eq. (1) as channel 1, and the apparent activation barrier  $E_{a2}$  was 5 eV. Channel 2 is considered to be dissociative adsorption from  $N_2$  in the ground state. The difference of the apparent activation barriers between the two channels, i.e.,  $E_{a2} - E_{a1} = 4$  eV, correlates with the difference between the dissociation energies of the ground and the excited states of a free molecule. This difference in a free molecule is 2.8 eV for  $a^1\Pi_g$  and 4.0 eV for  $B^3\Pi_g$  of the excited states.

We cannot reach a clear conclusion about the adsorption rate independent of the incidence angle as mentioned above. This seems to be a common feature characteristic of  $N_2$  molecules. Pfnür *et al.*<sup>22(c)</sup> discussed two possible models to account for the total energy scaling; one is the corrugated surface model and the other is the multiple encounter mod-

el.<sup>23</sup> From our explanation for Figs. 2 and 3, the former model is more reasonable. Namely, an incoming N<sub>2</sub> molecule interacts with a single Ni atom rather than an aggregate of Ni atoms due to the highly localized interaction between N<sub>2</sub> and Ni.<sup>34</sup> Hence, surface potential is considerably corrugated and the adsorption rate depends on the total energy.

In summary, we have observed unambiguously two dissociative adsorption processes of N<sub>2</sub> on Ni and we have arrived at the following interpretation: one channel is through N<sub>2</sub><sup>\*</sup> characterized by a low activation energy and the other channel through N<sub>2</sub> of a high activation energy. Mass-selected ion beams of very low energy can be used complementary with a usual molecular beam in the sense that the very-low-energy ion beam is actually equivalent to a neutral beam containing electronically excited species produced by resonance neutralization. The ability of the ion beam technique to prepare the beam over a wide energy range is attractive for studying various surface chemical processes, because the beam energy range is too wide to be produced by the molecular-beam technique in the present stage. Our result is consistent with the general perception that electronically excited molecules of N<sub>2</sub> and CO facilitate dissociative adsorption.

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