

## ON THE SELECTIVE ELIMINATION OF INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION USING STRONG RESONANT LASER FIELDS

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Received 18 March 1985

A method is proposed for the selective elimination of intramolecular vibrational redistribution (IVR) in polyatomic molecules by using a strong resonant laser excitation. When the Rabi frequency is larger than the frequency spread of an isolated group of molecular eigenstates, IVR processes are totally suppressed, and the molecule simply oscillates between the ground state and the doorway state. The method may have direct implications on laser-selective chemistry.

Laser excitation of polyatomic molecules (whether infrared or optical) is usually selective for short times. The dipole operator often has strict selection rules, which limit the states directly accessible to a small fraction of the available phase space. As time evolves, however, intramolecular vibrational redistribution (IVR) processes take place, and the initial selectivity is lost [1–3]. The chemical timing spectroscopy of Parmenter et al. [4] and experiments, which are both time- (picosecond) and frequency-resolved in supersonic beams [5,6], demonstrate this unambiguously. They show how the emission of an excited polyatomic molecule is simple and sharp at short times, which is characteristic of the doorway state. This simplicity is lost, however, at longer times, following the IVR processes. The basic problem in laser-selective chemistry is to find a method to overcome the IVR processes and to maintain the optical selectivity for times long enough for chemical processes to take place. In the absence of such a method, laser-induced chemical processes become statistical in nature and lose their selectivity. This is the situation, e.g., in the infrared multiphoton dissociation studies of polyatomic molecules [1,2].

In this Letter, we propose a way to eliminate IVR processes and achieve a laser-selective excitation by

using a strong on-resonance laser field. When the Rabi frequency of the excitation field is strong enough, we show that it will be selective and may overcome the IVR processes. We consider a molecular level scheme consisting of a vibronic ground state  $|g\rangle$  which is radiatively coupled to a single doorway state  $|s\rangle$ . The latter is, in turn, coupled via an intramolecular coupling  $V_{sI}$  to a manifold  $\{|I\rangle\}$  of  $N$  levels quasidegenerate with  $|s\rangle$ . The state  $|s\rangle$  and the  $N$   $\{|I\rangle\}$  states are assumed to form an isolated group of molecular states, well separated from all other molecular states. We shall assume that  $|s\rangle$  and  $\{|I\rangle\}$  are harmonic states, belonging to the same electronic state, and  $V_{sI}$  are anharmonicities. The model may correspond also to other physical situations, such as electronic to vibrational energy transfer, whereby  $|s\rangle$  and  $\{|I\rangle\}$  belong to different electronic states, and  $V_{sI}$  are non-adiabatic or spin-orbit couplings. We further assume, that the molecule interacts with a strong monochromatic laser field with frequency  $\omega_L$ . The total Hamiltonian for the molecule and the radiation field in the rotating wave approximation is [2,7]

$$H = H_0 + V, \quad (1)$$

where

$$H_0 = |g\rangle(E_g + \omega_L)\langle g| + |s\rangle E_s \langle s| + \mu E (|g\rangle\langle s| + |s\rangle\langle g|) + \sum_I |I\rangle E_I \langle I| \quad (1a)$$

<sup>1</sup> Camille and Henry Dreyfus Teacher-Scholar.

and

$$V = \sum_I (V_{sI}|s\rangle\langle I| + V_{Is}|I\rangle\langle s|). \quad (1b)$$

Here  $E_g$ ,  $E_s$ , and  $E_I$  are the energies of these states,  $\mu E$  is the transition dipole times the electric field, and  $V_{sI}$  is the intramolecular coupling. The Hamiltonian  $H_0$  (eq. (1a)) can be diagonalized exactly, resulting in

$$H_0 = |\phi_+\rangle E_+ \langle\phi_+| + |\phi_-\rangle E_- \langle\phi_-| + \sum_I |I\rangle E_I \langle I|, \quad (2)$$

where the eigenstates are

$$|\phi_+\rangle = \cos(\frac{1}{2}\theta) |g\rangle + \sin(\frac{1}{2}\theta) |s\rangle, \quad (3a)$$

$$|\phi_-\rangle = -\sin(\frac{1}{2}\theta) |g\rangle + \cos(\frac{1}{2}\theta) |s\rangle \quad (3b)$$

and where

$$\tan \theta = 2\mu E / (E_g + \omega_L - E_s), \quad (4a)$$

$$E_{\pm} = E_m \pm \frac{1}{2}\Omega, \quad (4b)$$

$$\Omega = [(\omega_{sg} - \omega_L)^2 + 4\mu^2 E^2]^{1/2}, \quad (4c)$$

$$E_m = \frac{1}{2}(E_g + E_s + \omega_L), \quad (4d)$$

$\Omega$  being the Raby frequency. We assume near resonance excitation, so that  $E_m \approx E_s$ . Let us consider now the limit of a strong resonant excitation, i.e.

$$\mu E \gg \omega_{sg} - \omega_L, V_{sI}, \omega_{sI}, \quad (5)$$

where  $\omega_{\alpha\beta} \equiv E_{\alpha} - E_{\beta}$ . In this case,  $\theta = \pi/2$ , resulting in

$$|\phi_+\rangle = 2^{-1/2}(|s\rangle + |g\rangle), \quad (6a)$$

$$|\phi_-\rangle = 2^{-1/2}(|s\rangle - |g\rangle) \quad (6b)$$

and

$$\Omega = 2\mu E. \quad (6c)$$

Suppose the molecule is initially in the ground state  $|g\rangle$ . At time  $t = 0$  the radiation field is turned on. The molecular wavefunction at time  $t$  will then be given by

$$|\Psi(t)\rangle = U(t) |g\rangle, \quad (7)$$

where  $U(t)$  is the time evolution operator

$$U(t) = \exp(-iHt). \quad (8)$$

We shall be interested in the time-dependent prob-

ability of the molecule to be in the states  $|g\rangle$ ,  $|s\rangle$ , and in the quasicontinuum  $\{|I\rangle\}$ , i.e.

$$P_g(t) \equiv |\langle g|U(t)|g\rangle|^2, \quad (9a)$$

$$P_s(t) \equiv |\langle s|U(t)|g\rangle|^2 \quad (9b)$$

and

$$P_I(t) \equiv \sum_{I'} |\langle I'|U(t)|g\rangle|^2. \quad (9c)$$

In order to show how the selective elimination of IVR takes place, we shall rewrite  $U(t)$  in the interaction picture [7]:

$$U(t) = \exp(-iHt) = \exp(-iH_0t) \exp_+ \left( -i \int_0^t d\tau V_I(\tau) \right), \quad (10)$$

where  $V_I(\tau)$  is  $V$  in the interaction picture,

$$V_I(\tau) = \exp(iH_0\tau) V \exp(-iH_0\tau) \quad (11a)$$

and  $\exp_+$  is the positive time-ordered exponential

$$\begin{aligned} \exp_+ \left( -i \int_0^t d\tau V_I(\tau) \right) &= 1 - i \int_0^t d\tau V_I(\tau) \\ &+ (-i)^2 \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 V_I(\tau_1) V_I(\tau_2) + \dots \end{aligned} \quad (11b)$$

Making use of the Magnus expansion [8], we can rearrange eq. (10) in the form

$$U(t) = \exp(-iH_0t) \exp[F(t)], \quad (12)$$

where

$$\begin{aligned} F(t) &= -i \int_0^t d\tau V_I(\tau) \\ &- \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 [V_I(\tau_1), V_I(\tau_2)] + \dots \end{aligned} \quad (12a)$$

In order to evaluate eq. (12) explicitly, we shall use the eigenstates of  $H_0$ , so that

$$\begin{aligned} V_I(\tau) &= \sum_I V_{sI} \exp(i\omega_{mI}\tau) \\ &\times [|s\rangle\langle I| \cos(\frac{1}{2}\Omega\tau) + |g\rangle\langle I| \sin(\frac{1}{2}\Omega\tau)] + \text{h.c.}, \end{aligned} \quad (13)$$

where  $\omega_{mI} \equiv E_m - E_I$ . For a strong field  $\Omega \gg V_{sI}$ ,  $\omega_{mI}$  (eq. (5)). In this case, the oscillation frequency of  $V_I$  (i.e.  $\Omega$ ) is much larger than the magnitude of  $V_I$  (i.e.  $V_{sI}$ ). The time integrals (eq. (12a)) on the rele-

vant time scale  $\tau \sim V_{sl}^{-1}$  then vanish, and  $F(t)$  is being averaged to zero. The effect of  $V_1$  can be made as small as desirable by increasing  $\Omega$ . In this limit, we therefore get

$$F(t) \approx 0 \quad (14a)$$

and

$$U(t) = \exp(-iH_0 t). \quad (14b)$$

$V_{sl}$  was therefore averaged to zero. Making use of eqs. (2), (12) and (14) we finally get

$$P_s(t) = \sin^2(\frac{1}{2}\Omega t), \quad (15a)$$

$$P_g(t) = \cos^2(\frac{1}{2}\Omega t) \quad (15b)$$

and

$$P_l(t) = 0. \quad (15c)$$

The population simply oscillates rapidly between levels  $|s\rangle$  and  $|g\rangle$ , and levels  $\{|l\rangle\}$  are never populated. Under these conditions, IVR processes, which would normally populate the  $\{|l\rangle\}$  manifold, are totally eliminated. The elimination of IVR is analogous to the selective averaging in magnetic resonance [9] and to the elimination of  $T_2$  processes in strong radiation fields [10,11]. For the sake of comparison, let us consider the same molecular system interacting with a weak and pulsed radiation field, i.e.

$$\mu E = \phi(t) \exp(-i\omega_L t) + \text{c.c.}, \quad (16)$$

where  $\phi(t)$  denotes the transition dipole times the field amplitude. In this case, to lowest order in the field amplitude  $\phi(t)$ , we have [12]:

$$P_s(t) = |C_s(t)|^2, \quad (17a)$$

$$P_l(t) = \sum_{l'} |C_{l'}(t)|^2 \quad (17b)$$

and

$$P_g(t) = 1 - P_s(t) - P_l(t), \quad (17c)$$

where the amplitudes  $C_s$  and  $C_{l'}$  are given by

$$C_s(t) = -i \int_0^t d\tau G_{ss}(\tau) \exp[-i(E_g + \omega_L)(t - \tau)] \times \phi(t - \tau), \quad (18a)$$

$$C_{l'}(t) = -iV_{l's} \int_0^t d\tau \exp[-iE_{l'}(t - \tau)] C_s(\tau). \quad (18b)$$

The Green's function  $G_{ss}(\tau)$  may be calculated using the molecular eigenstates  $|j\rangle$ , which diagonalize the molecular Hamiltonian  $H_M$  (eq. (1) with  $\mu = 0$ )

$$H_M = |g\rangle(E_g + \omega_L)\langle g| + |s\rangle E_s \langle s| + \sum_l |l\rangle E_l \langle l| + \sum_l (V_{sl}|s\rangle\langle l| + V_{ls}|l\rangle\langle s|), \quad (19)$$

i.e.

$$H_M |g\rangle = (E_g + \omega_L) |g\rangle, \quad (20a)$$

$$H_M |j\rangle = E_j |j\rangle, \quad (20b)$$

where

$$|j\rangle = \alpha_j |s\rangle + \sum_l \beta_{lj} |l\rangle \quad (21)$$

and where

$$G_{ss}(\tau) = \sum_j |\alpha_j|^2 \exp(-iE_j \tau). \quad (22)$$

Eqs. (17), (18), and (22) usually predict fast IVR processes, whereby the excited-state population relaxes to the quasicontinuum, and  $P_l$  grows with time. This is in marked contrast to eqs. (15), which predict no IVR in the presence of a strong radiation field.

In order to illustrate the variation of IVR with the Rabi frequency, we have performed some numerical computations. We considered a level scheme consisting of 100 equally spaced  $|l\rangle$  levels. The excitation frequency was turned on resonance with the doorway state, and the coupling matrix elements  $V_{sl}$  were taken to be random variables bounded between  $\pm W$ , i.e.

$$E_s = E_g + \omega_L = 0, \quad (23)$$

$$-\frac{1}{2}\Delta < E_l < \frac{1}{2}\Delta, \quad -W < V_{sl} < W.$$

We have chosen  $\Delta = 100$ ,  $W = 3$ , and the spacing between adjacent  $|l\rangle$  levels was 1.  $H_M$  was diagonalized numerically, resulting in the eigenvectors  $|j\rangle$  and eigenvalues  $E_j$ .

The ordinary (weak field) absorption lineshape of this system is

$$I_a(\omega_L) = \sum_j |\alpha_j|^2 \delta(\omega_{jg} - \omega_L) \quad (24)$$

and is shown in fig. 1. In fig. 2 we show  $P_l(t)$  calculated for a conventional  $\delta$  function excitation ( $\phi(t) =$

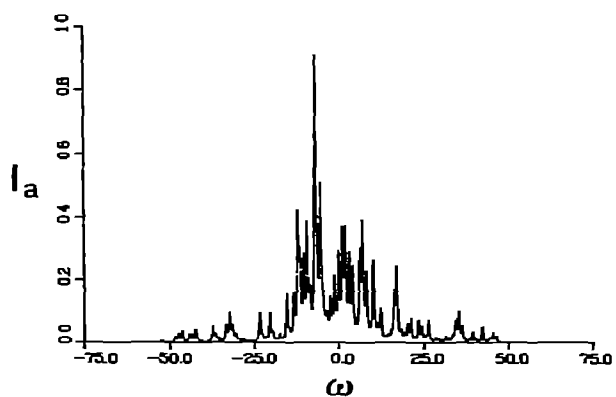


Fig. 1. The absorption lineshape (eq. (24)) for our model system with 100  $h$  levels  $\Delta = 100$ ,  $W = 3$ . A radiative width  $\gamma = 0.5$  was assumed for all levels.

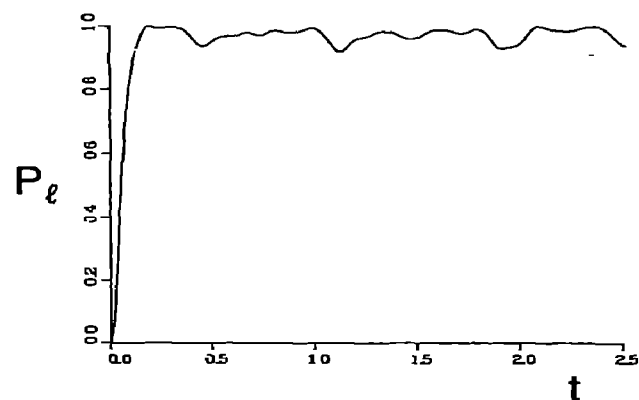


Fig. 2.  $P_l(t)$  for a short pulsed excitation, where  $P_s(0) = 1$  (eq. (25b)). The level scheme is the same as in fig. 1 with  $\gamma = 0$ .

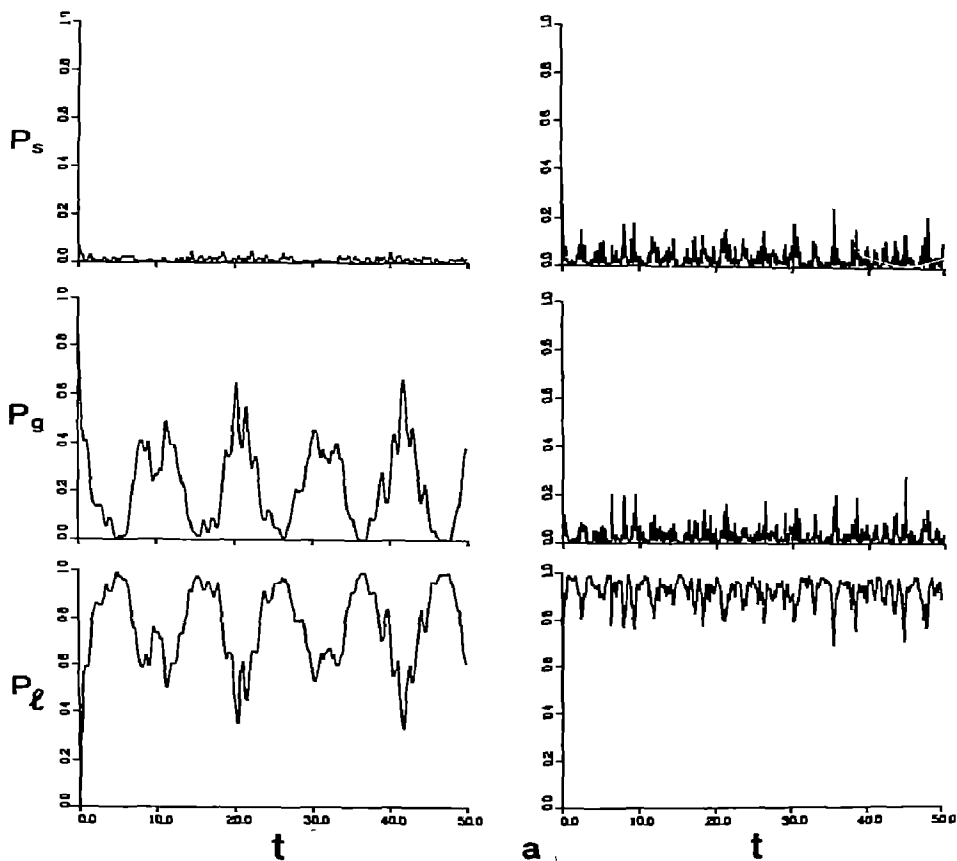


Fig. 3a

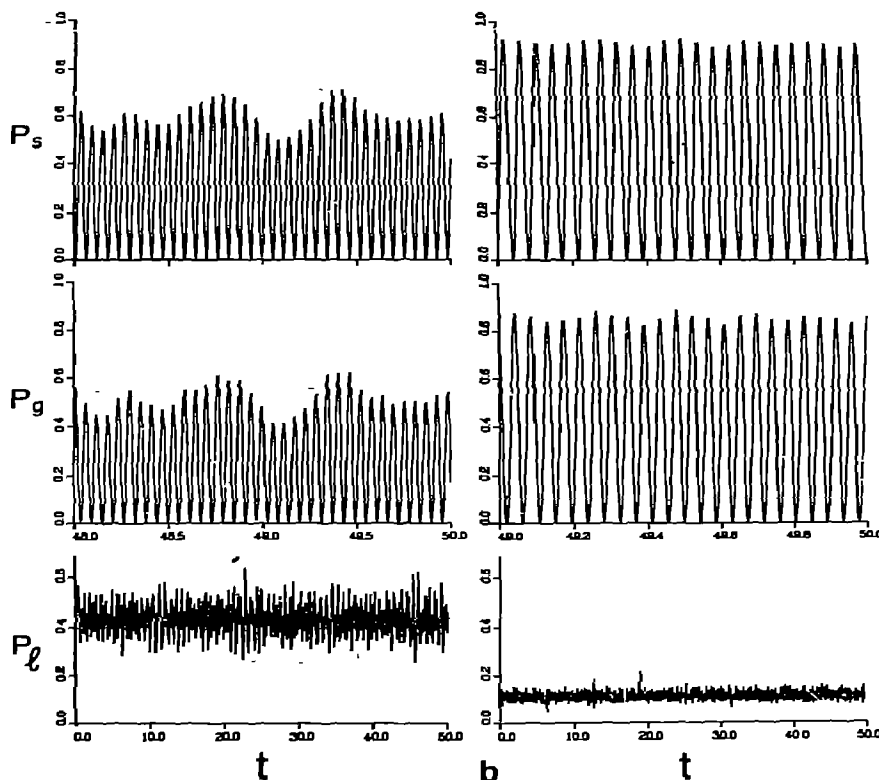


Fig. 3. (a)  $P_s(t)$ ,  $P_g(t)$ , and  $P_l(t)$  (eq. (9)) for the model system of fig. 2 with  $\Omega = 3$  (left column) and  $\Omega = 20$  (right column). IVR is clearly seen. (b) Same as (a) but for  $\Omega = 50$  (left column) and  $\Omega = 70$  (right column). The IVR is totally eliminated in these cases.

$\delta(\tau)$  in eq. (18a)). In this case, we prepare the doorway state at  $t = 0$ ,  $P_s(0) = 1$ , and we have

$$P_s(t) = |G_{ss}(t)|^2 \quad (25a)$$

and

$$P_l(t) = 1 - |G_{ss}(t)|^2, \quad (25b)$$

where  $G_{ss}(t)$  is given by eq. (22). It is clear from fig. 2 that on a time scale of  $t \approx 0.1$  IVR is essentially completed, and the population relaxes to the  $\{|I\rangle\}$  manifold. In fig. 3 we consider a stationary excitation field with a Rabi frequency of  $\Omega = 3, 20, 50$ , and  $70$ . The calculations were made using eqs. (9), and  $U(t)$  was evaluated by diagonalizing the Hamiltonian  $H$  (eq. (1)) corresponding to the molecule and the radiation field. For small Rabi frequencies ( $\Omega = 3, 20$ )

there is a fast IVR, and  $P_l(t)$  oscillates around 1. This is qualitatively similar to fig. 2. As  $\Omega$  is increased, the IVR is suppressed, and the  $\Omega = 70$  case behaves closely to what is predicted by eqs. (15). In fig. 4 we show  $P_l(t)$  for several values of  $\Omega$ . Fig. 4 demonstrates that the elimination of IVR occurs quite sharply, as  $\Omega$  becomes comparable to  $\frac{1}{2}\Delta$ , since then the eigenstates  $|\phi_+\rangle$  and  $|\phi_-\rangle$  with eigenvalues  $\approx \pm\Omega$  are detuned outside the range  $\Delta$ . This state of affairs may provide an opportunity for performing laser-selective chemistry, since the selectivity is maintained for very long times. (As long as the excitation field is on) A second laser field, which interacts with the  $|s\rangle$  state, may result in a selective predissociation, isomerization, etc without the participation of the  $\{|I\rangle\}$  manifold.

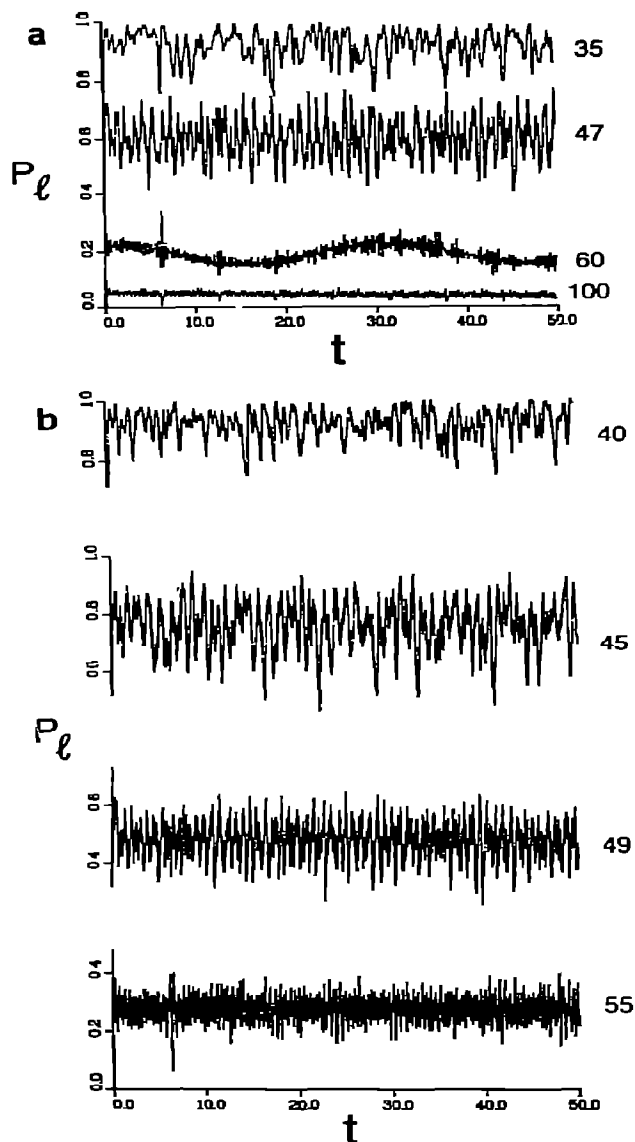


Fig. 4  $P_l(t)$  for various values of  $\Omega$  (indicated in each plot). Other parameters are the same as of fig. 2. (b) demonstrates that the elimination of IVR with  $\Omega$  occurs sharply as  $\Omega \approx \frac{1}{2}\Delta$ .

The support of the National Science Foundation, the Office of Naval Research, the Army Research Office, and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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