

**The effect of initial S 1 vibrational mode on the photodissociation  $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$**

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## COMMUNICATIONS

## The effect of initial $S_1$ vibrational mode on the photodissociation $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}^a$

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Photodissociation dynamics of  $\text{H}_2\text{CO}$  have been much studied in recent years because of the experimental feasibility for the state-selective excitation and the determination of the nascent product state distribution. Additionally, there has been considerable theoretical interest in treating this polyatomic dissociation problem, and recent reviews provide significant progress made through 1982 on formaldehyde photochemistry<sup>1</sup> and spectroscopy.<sup>2</sup> More recently, the experimental studies on the energy partitioning for the  $\text{H}_2 + \text{CO}$  product channel have revealed low translational excitation,<sup>3</sup> moderate rotational and vibrational excitation in  $\text{H}_2$ ,<sup>4</sup> and high rotational and low vibrational excitation in  $\text{CO}$ .<sup>5</sup> These findings are thought to be consistent with the theoretical description of the  $S_0$  dissociation model which gives a nonstatistical state distribution often associated with dynamical effects in the exit channel.<sup>6</sup> Below and near the dissociation threshold, quantum mechanical calculations involving the asymmetric, planar transition state<sup>7-9</sup> and the tunneling through the barrier<sup>10</sup> have predicted state-specific rates when limited coupling exists between different vibrational motions. Recent studies on the Stark tuning of the  $S_1$  and  $S_0$  levels support strongly the state-specific rate behavior, suggestive of mode specificity.<sup>11,12</sup> Among the few important questions remaining to be answered<sup>4-11</sup> is the effect of initial  $S_1$  vibrational mode on the photodissociation. In this paper, we wish to present direct experimental evidence that the "out-of-plane" mode ( $\nu_4'$ ) in  $S_1$  couples to the molecular dissociation coordinate in  $S_0$  several times more effectively than the "in-plane" modes ( $\nu_5'$  and  $\nu_6'$ ) in  $S_1$ .

The key to the above supposition is provided by a comparison study of the  $S_1$  lifetimes ( $\tau_F$ ) of the jet-cooled, low-lying  $J', K'$  levels of the nearly isoenergetic single vibronic levels (SVL's) having the excitation of an in-plane vibrational mode, i.e., the antisymmetric C-H stretch ( $\nu_5'$ ) or the in-plane  $\text{CH}_2$  wag ( $\nu_6'$ ) vs the out-of-plane  $\text{CH}_2$  wag ( $\nu_4'$ ). Because the vibronic transition intensity involving  $\nu_4' = \text{odd}$  is considerably stronger than that involving  $\nu_5' = \text{odd}$  or

$\nu_6' = \text{odd}$ , the key experiments described here have become possible only recently with the jet-cooling LIF techniques.<sup>13,14</sup> The range of the lifetime variation for a set of  $\sim 10$  low-lying asymmetric rotor levels of SVL's is summarized in Fig. 1 for  $5^1$  vs  $1^4 1^1$ , together with the recently published data on the  $2^1 6^1$  vs  $2^1 4^3$  comparison,<sup>13</sup> the  $6^1$  vs  $4^3$  comparison,<sup>15(a),15(b)</sup> and the  $4^1$  and  $2^4 1^1$  levels<sup>15(c)</sup> as a function of the excess vibrational energy ( $E'_{\text{vib}}$ ). Some of the  $S_1$  lifetimes measured at room temperature<sup>16-18</sup> for sampling a wide range of rotational quantum numbers,  $J' = 0-15$  and  $K' = 0-8$ , are included in Fig. 1 in order to show the smooth trend with  $E'_{\text{vib}}$ . The jet-cooled  $S_1$  lifetimes of  $2^1 4^3$  and  $1^4 1^1$  were shorter than 15 ns comparable to the corresponding room temperature values.

The jet-cooled levels sample the range of  $J' = 0-4$  and  $K' = 0-2$  (4-10 K) for which the Coriolis effect is almost negligible and therefore show the "pure" SVL properties, nearly free from the rotation-induced effect,<sup>19-21</sup> unless a complication due to Fermi-resonance is introduced. The Coriolis-induced vibrational mixing and its effect on the  $S_1$  lifetime will be fully treated with a separate publication in the future. However, it should be mentioned here that the random scatter in a plot of  $\tau_F$  vs  $J'$ , which is due to the presence of the lumpy continuum,<sup>1,16</sup> decreases gradually with  $E'_{\text{vib}}$  but persists even up to  $E'_{\text{vib}} \approx 3000 \text{ cm}^{-1}$ . It is seen clearly in Fig. 1 that our jet-cooled lifetime values of  $5^1$  are  $\sim 4$  times longer than those of  $1^4 1^1$ , and similarly  $\tau_F(2^1 6^1)$  is three times longer than  $\tau_F(2^1 4^3)$ . The data of Henke *et al.* also show that  $\tau_F(6^1)$ 's are several times longer than  $\tau_F(4^3)$ 's. While there is a definite trend for decreasing  $S_1$  lifetime with increasing  $E'_{\text{vib}}$ , clearly there are two distinct series (even for the room temperature samples). The  $2^4 1^1$  and  $2^4 3^1$  levels with the excitation of the out-of-plane mode ( $\nu_4'$ ) undergo the  $S_1 \rightarrow S_0$  radiationless transition at least three times faster than the  $2^6 1^1$  and  $2^5 1^1$  levels with the excitation of the in-plane mode ( $\nu_5'$  and  $\nu_6'$ ).

The electronic state symmetries of  $S_0$  and  $S_1$   $\text{H}_2\text{CO}$  are

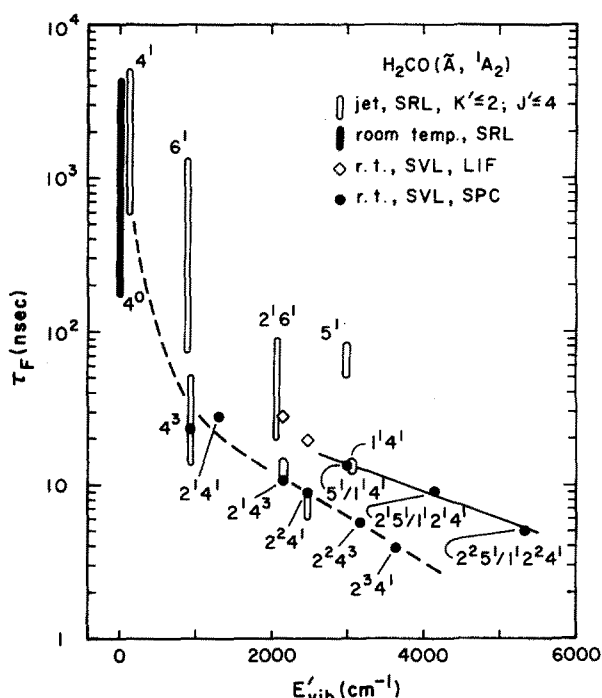


FIG. 1. The collision-free  $S_1$  lifetimes of single vibronic levels measured by a variety of experiments are shown as a function of excess vibrational energy ( $E'_{\text{vib}}$ ):  $\circ$  Jet-cooled SVL values for the range of  $J' = 0-4$  and  $K' = 0-2$  [ $2^1 4^1$  from Selzle and Schlag [Ref. 15(c)];  $4^1$ ,  $4^3$ , and  $6^1$  from Henke and Schlag [Refs. 15(c) and 15(b)];  $2^1 6^1$  and  $2^1 4^3$  from Apel and Lee (Ref. 13);  $5^1$  and  $1^1 4^1$  from this work];  $\bullet$  SRL values at room temperature [ $4^0$  from Weisshaar and Moore (Ref. 16)];  $\diamond$  rotationally unresolved SVL values at room temperature [ $2^1 4^3$  and  $2^2 4^1$  from Yeung and Moore (Ref. 17)];  $\bullet$  rotationally unresolved SVL values at room temperature [Miller and Lee (Ref. 18) 2 ns  $D_2$  flash lamp/single photon counting]—the  $2^2 5^1/1^1 2^2 4^1$  Coriolis interacting pair were not resolved.

$A_1$  and  $A_2$ , respectively, and the three nontotally symmetric vibrational species are  $\nu_4(b_1)$ ,  $\nu_5(b_2)$ , and  $\nu_6(b_2)$ .  $\text{H}_2\text{CO}$  has no vibrational fundamental of  $a_2$  symmetry. Therefore, to preserve the vibronic symmetries of  $S_1$  and  $S_0$  (in  $C_{2v}$ ), group theory requires the following relationship; (a) if  $\Gamma_v(S_1) = b_1$ , then for  $S_0$ ,  $\nu_4'' = \text{even}$  and  $\nu_5'' + \nu_6'' = \text{odd}$ ; (b) if  $\Gamma_v(S_1) = b_2$ , then  $\nu_4'' = \text{odd}$  and  $\nu_5'' + \nu_6'' = \text{even}$ . When  $S_1$  has an excitation of  $\nu_4' = \text{odd}$ , then  $S_0$  must contain an excitation of  $\nu_5''$  or  $\nu_6''$  which is the in-plane, antisymmetric vibrational mode effective for dissociation.<sup>10</sup> On the other hand, when  $S_1$  has an excitation of  $\nu_5' = 1$  or  $\nu_6' = 1$ , then  $S_0$  need not contain an excitation of  $\nu_5''$  and  $\nu_6''$ . The observed  $S_1$  vibrational mode dependence is consistent with the above explanation based on the  $S_0$  vibrational mode specificity obtained theoretically.<sup>7-10</sup> However, one should be cautioned that the symmetry restriction breaks down when the  $\text{H}_2\text{CO}$  molecule rotates and the vibrational symmetry is compromised by

Coriolis interaction.<sup>19-22</sup> The mode specificity shown here should be further verified by the state selective studies of the  $S_1$  level excitation with  $\nu_5' = 1$  or  $\nu_6' = 1$  by Stark tuning as well as by nascent product state distribution probing.

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