APPENDIX E

TARGET AND REFERENCE WAVE PACKETS

Here we derive analytic expressions for the target (reference) wave packet defined by Eq. (5.25) (Eq. (5.26)). Using the short-pulse limit of the B_x pulse propagator (5.11) and the free-evolution operator of first-order in J given in footnote 52 of Chapter V, we find

$$\left|\ {}_1 \right\rangle = \frac{J}{2} area_B \ {}_0^{t_w} d \quad e^{\ iH_1\,(t_w \quad)} e^{\ iH_1} \left|0,0\right\rangle \ . \tag{E.1}$$

The target wave packet (E.1) is assumed to originate from the vibrational ground-state of the electronically unexcited complex; $area_I = \quad dt\, A_I(t)$ is the integrated pulse envelope.

We can use harmonic-oscillator creation and annihilation operators to go further with Eq. (E.1). Adopting the usual definitions $q_a = (2m \quad)^{\ 1/2}(a^\dagger + a)$, $p_a = i(m \quad /2)^{1/2}(a^\dagger \quad a)$, $q_b = (2m \quad)^{\ 1/2}(b^\dagger + b)$, $p_b = i(m \quad /2)^{1/2}(b^\dagger \quad b)$, and introducing the corresponding phase-space translation operators $T_a(\ \ ) = \exp(\ \ a^\dagger \qquad {}^* a)$ and $T_b(\ \ ) = \exp(\ \ b^\dagger \qquad {}^* b)$, we have

$$H_1 = T_a(\ \ )(H_0 + \ \ {}_1)T_a^\dagger(\ \ ) \tag{E.2}$$

$$H_1 \ = T_b(\ \ )(H_0 + \ \ {}_1)T_b^\dagger(\ \ ) \tag{E.3}$$

$$H_2 = T_a(\ \ )T_b(\ \ )(H_0 + \ \ {}_2)T_b^\dagger(\ \ )T_a^\dagger(\ \ ) \ . \tag{E.4}$$

From the relations (E.1) through (E.4) and some operator algebra it follows that

$$\left|\ {}_{1}\right\rangle = \frac{J}{2} area_B e^{\ 2\ \ 2\quad i\ 1\ \ vib/2} \tag{E.5}$$

$$\int_0^{vib/2} d\ \ \exp\{i(\ _1 \quad _1) \quad 2i\ ^2 \sin \quad + \ (1 \quad e^{i}\quad)a^{\dagger} + \ (1+e^{i}\quad)b^{\dagger}\}\left|0,0\right\rangle .$$

The dimensionless displacement is $\ = (m \quad /2)^{1/2} d$, and the waiting time has been set to $t_w = \ \ _{vib}/2$.

In the short-pulse limit, the reference wave packet (5.26) prepared from the vibronic ground state remains a quasi-classical coherent state of the form

$$\left|\ {}_{1}\right\rangle = \ i \ \frac{}{2}^{\,3} area_A area_C area_D e^{i\ \ _p t_p\ \ i\ \ _d t_d} e^{iH_2 t_d} e\ ^{iH_1 (t_p + t_w + t_d)} e^{iH_0 t_p} \left|0,0\right\rangle \ . \tag{E.6}$$

Relations (E.3) and (E.4) plus some operator manipulations (and the choice $t_w = \ \ _{vib}/2$) lead to the more explicit expression

$$\left|\ {}_{1}\right\rangle = i\ \frac{}{2}^{\,3} area_A area_C area_D \tag{E.7}$$

$$\exp \quad i \frac{\ _1\ \ _{vib}}{2} + i(\ \ _p \quad \ _1)t_p \quad i(\ \ _d + \ \ _1 \quad \ _2)t_d$$

$$+ \ ^2 e^{i\ \ t_d} \quad ^2 e^{\ i\ \ t_p} \quad 2\ \ ^2 + \ (1 \quad e^{i\ \ t_d})a^{\dagger} + \ (1 + e^{\ i\ \ t_p})b^{\dagger}\Big\}\left|0,0\right\rangle .$$

The inner product of (E.5) and (E.7) leads to the experimentally isolable complex overlap, Eq. (5.29), that is plotted in Chapter V.