APPENDIX F

INTERFEROGRAM FRINGE STRUCTURE

In order to better understand the local fringe structure of the peaks in the 2D interferograms presented for the case of an energy-transfer complex in Chapter V, it is useful to consider the first derivatives with respect to t_p and t_d of the complex overlap between the target (5.25) and reference (5.26) wave packets. In the short-pulse limit adopted there, the reference wave packet (though not the target) prepared from the vibrational ground state is a minimum-uncertainty Gaussian wave packet,

$$\langle q_a, q_b | \quad {}_1 \rangle \tag{F.1}$$

$$= \exp \quad \frac{m}{2}(q_a \quad \bar{q}_a)^2 \quad \frac{m}{2}(q_b \quad \bar{q}_b)^2 + i\bar{p}_a(q_a \quad \bar{q}_a) + i\bar{p}_b(q_b \quad \bar{q}_b) + i$$

whose time evolution is governed by the quasiclassical motion of the average values of the position and momentum expectation values

$$\bar{q}_a \quad \frac{\langle \quad {}_1 | q_a | \quad {}_1 \rangle}{\langle \quad {}_1 | \quad {}_1 \rangle} = d(1 \quad \cos \quad t_d) \tag{F.2}$$

$$\bar{p}_a \quad \frac{\langle \quad {}_1 | p_a | \quad {}_1 \rangle}{\langle \quad {}_1 | \quad {}_1 \rangle} = \quad m \quad d \sin \quad t_d \tag{F.3}$$

$$\bar{q}_b \quad \frac{\langle \quad {}_1 | q_b | \quad {}_1 \rangle}{\langle \quad {}_1 | \quad {}_1 \rangle} = d(1 \quad \cos \quad (t_w + t_p)) \tag{F.4}$$

$$\bar{p}_b \quad \frac{\langle \ _1 | p_b | \ _1 \rangle}{\langle \ _1 | \ _1 \rangle} = m \quad d \sin \quad (t_w + t_p) \tag{F.5}$$

and the (complex) phase

$$= \ _0 \quad \frac{}{2} \quad i \ln \pm \frac{}{2} \quad {}^3 \quad area_A area_C area_D \quad + \quad _p t_p \quad \quad _d t_d + \ _p \quad \ _p \tag{F.6}$$

$$t_w \quad \ _1 (t_d + t_w + t_p) + \ _2 t_d + \frac{m \quad d^2}{4} \left(\sin 2 \quad t_d \quad \sin 2 \quad (t_w + t_p) \right).$$

Contributions from the short-pulse limit of the pulse propagators (5.11) have been included in Eq. (F.6); $_0$ is the arbitrary initial phase attached to $\langle q_a, q_b | n_0 \rangle$. The wave function (F.1) is the position-space representation of (E.7).

Writing the target-reference overlap in terms of a complex phase, $\langle \ _{1'} | \ _{1'} \rangle = \exp(i \quad)$, leads to the sought-for time derivatives

$$\frac{}{t_p} = \quad _p + \ _1 + \frac{m \quad {}^2 d^2}{2} \quad m \quad {}^2 d e^{i \quad (t_w + t_p)} \frac{\langle \ _1 | q_b \quad \bar{q}_b | \ _1 \rangle}{\langle \ _1 | \ _1 \rangle} \tag{F.7}$$

$$\frac{}{t_d} = \quad _d + \ _1 \quad \ _2 \quad \frac{m \quad {}^2 d^2}{2} + m \quad {}^2 d e^{i \quad t_d} \frac{\langle \ _1 | q_a \quad \bar{q}_a | \ _1 \rangle}{\langle \ _1 | \ _1 \rangle} \tag{F.8}$$

As could have been anticipated from Fig. 5.3, the derivative with respect to t_d (t_p) is sensitive to only the donor (acceptor) vibration. The interferogram fringe structure yields information on the spatial form of the target energy-transfer amplitude through the last term on the right-hand side of Eqs. (F.7) and (F.8).

Our closed-form expression for $\langle \ _1 | \ _1 \rangle$ gives equivalent alternative forms for the delay derivatives of . By differentiation of Eq. (5.29) we obtain

$$\frac{}{t_p} = i\frac{\langle\ _1 \mid\ _1\rangle / \ t_p}{\langle\ _1 \mid\ _1\rangle} = \ _p + \ _1 + \ ^2 e^{i\ t_p} R \tag{F.9}$$

and

$$\frac{}{t_d} = i\frac{\langle\ _1 \mid\ _1\rangle / \ t_d}{\langle\ _1 \mid\ _1\rangle} = \ _d + \ _1 \ \ _2 \ \ ^2 e^{i\ t_d} R \tag{F.10}$$

where, in both cases,

$$R = \frac{{}_0^{vib/2} d \ \exp\{i(\ _1 \ \ _1 + \ ) + \ ^2 e^{i} \ (e^{i\ t_p} + e^{i\ t_d} \ 1) + \ ^2 e^{i} \ \ 2 \ ^2\}}{{}_0^{vib/2} d \ \exp\{i(\ _1 \ \ _1) + \ ^2 e^{i} \ (e^{i\ t_p} + e^{i\ t_d} \ 1) + \ ^2 e^{i} \ \ 2 \ ^2\}}. \tag{F.11}$$

Since the same ratio R appears in both (F.9) and (F.10), and the integrand in the numerator of (F.11) simply contains an extra factor $\exp(i \ \ )$, we have the remarkable result

$$\frac{e^{i\ (t_p + t_d)}}{2} \ \ _d + \ _1 \ \ _2 + i\frac{+}{t_d}\langle\ _1 \mid\ _1\rangle_{1,\ 1,\ 2} \tag{F.12}$$

$$= \frac{1}{2} \ \ _p + \ _1 \ \ i\frac{+}{t_p}\langle\ _1 \mid\ _1\rangle_{1,\ 1,\ 2} = \langle\ _1 \mid\ _1\rangle_{1,\ 1+\ ,\ 2+} \ .$$

The rate of change of the interferogram along either time axis specifies the complex-valued interference signal from a *different energy-transfer complex* with the acceptor and two-exciton site energies increased by one vibrational quantum. We have used Eq. (F.12) as a consistency check on the t_p and t_d fringe structure of the calculated interferograms presented in Chapter V.