APPENDIX I: SUPPLEMENTARY DISCUSSIONS

2DHETCOR without Δ_1

It is stated in Part I, Section 3.7, that in order to understand the role of the delay Δ_1 (see Figure I.2) we should carry on the calculations without it. We do this here.

We start by writing the density matrix before the combined 90*xCH* pulse:

$$D(5) = \begin{bmatrix} 3 & 0 & F & 0 \\ 0 & 2 & 0 & G \\ F* & 0 & 3 & 0 \\ 0 & G* & 0 & 2 \end{bmatrix} \qquad \text{(I1)}$$

If we have the delay Δ_1 = 1/2J, the expressions for F and G are taken from (I.32):

$$\begin{aligned} F &= d_{13}(5) = -2\exp[-i\Omega_H(t_e + \Delta_1)] \\ G &= d_{24}(5) = -F \end{aligned} \qquad \text{(I2)}$$

If Δ_1 is not used, the expressions for F and G, taken from (I.25) and (I.26), are:

$$F = d_{13}(4) = -2i\exp(-i\Omega_H t_e) = G \qquad \text{(I3)}$$

We apply the operator R_{90xCH} given in (I.34) to D(5) in (I1).

$$D(5)R_{90xCH} = \frac{1}{2}\begin{bmatrix} 3+iF & 3i-F & 3i+F & -3+iF \\ 2i-G & 2+iG & -2+iG & 2i+G \\ 3i+F* & -3+iF* & 3+iF* & 3i-F* \\ -2+iG* & 2i+G* & 2i-G* & 2+iG* \end{bmatrix}$$

Premultiplication with R_{90xCH}^{-1} gives the following expression for D(7)

$$\frac{1}{4}\begin{bmatrix} 10+i(F+G-F^*-G^*) & 2i-F+G+F^*-G^* & F+G+F^*+G^* & i(F-G+F^*-G^*) \\ -2i+F-G-F^*+G^* & 10+i(F+G-F^*-G^*) & -i(F-G+F^*-G^*) & F+G+F^*+G^* \\ F+G+F^*+G^* & i(F-G+F^*-G^*) & 10-i(F+G-F^*-G^*) & 2i+F-G-F^*+G^* \\ -i(F-G+F^*-G^*) & F+G+F^*+G^* & -2i-F+G+F^*-G^* & 10-i(F+G-F^*-G^*) \end{bmatrix}$$

(I4)

Now we can see why having $G = F$ is counterproductive. The factors F and G contain the proton information [see (I3)] and, when they are equal, this information disappears from the observable single-quantum coherences d_{12} and d_{34}. In this case $D(7)$ becomes

$$D(7)=\frac{1}{2}\begin{bmatrix} 5+iF-iF^* & 2i & F+F^* & 0 \\ -2i & 5+iF-iF^* & 0 & F+F^* \\ F+F^* & 0 & 5-iF-iF^* & 2i \\ 0 & F+F^* & -2i & 5-iF-iF^* \end{bmatrix}$$

(I5)

No pulse follows after $t(7)$ and each matrix element evolves in its own "slot." The matrix elements d_{12} and d_{34}. will be affected by the carbon evolution during the detection t_d (preceded or not by the coupled evolution Δ_2) but they will not be proton modulated. We will not have a 2D.

The DM calculations in Sections 3.6 to 3.9 have been carried on *with* the delay Δ_1 = 1/2J, i.e, with G = − F [see (I2)]. In this case D(7) is

$$D(7)=\frac{1}{2}\begin{bmatrix} 5 & i-F+F^* & 0 & i(F+F^*) \\ -i+F-F^* & 5 & -i(F+F^*) & 0 \\ 0 & i(F+F^*) & 5 & i+F-F^* \\ -i(F+F^*) & F+F^* & -i-F+F^* & 5 \end{bmatrix} \tag{I6}$$

Taking *F* from (I2) and using the notations (I.31)

$$c=\cos[\Omega_H(t_e+\Delta_1)]$$
$$s=\sin[\Omega_H(t_e+\Delta_1)]$$

we obtain

$$\begin{aligned} F &= -2(c-is) \\ F-F^* &= 4is \\ F+F^* &= -4c \end{aligned} \tag{I7}$$

By introducing (I7) into (I6) we can verify the expression of $D(7)$ given in (I.35). The carbon observables d_{12} and d_{34} contain now the factor *s* which carries the proton information. The role of the subsequent coupled evolution Δ_2 is explained in Section 3.9.

2DHETCOR without the 180*xC* pulse

We demonstrate here the result (I.51). The density matrix at $t(1)$, taken from (I.12), is

$$D(1) = \begin{bmatrix} 2 & 0 & -2i & 0 \\ 0 & 3 & 0 & -2i \\ 2i & 0 & 2 & 0 \\ 0 & 2i & 0 & 3 \end{bmatrix} \quad \text{(I8)}$$

Since the 180*xC* pulse and the delay Δ_1 are suppressed, all we have between $t(1)$ and $t(5)$ is an evolution t_e. The density matrix just before the 90*xCH* pulse is then

$$D(5) = \begin{bmatrix} 2 & 0 & B & 0 \\ 0 & 3 & 0 & C \\ B* & 0 & 2 & 0 \\ 0 & C* & 0 & 3 \end{bmatrix} \quad \text{(I9)}$$

with

$$\begin{aligned} B &= -2i\exp(-i\Omega_{13}t_e) \\ C &= -2i\exp(-i\Omega_{24}t_e) \end{aligned} \quad \text{(I10)}$$

We apply the 180*xCH* operator to (I9).

$$D(5)R_{90xCH} = \frac{1}{2}\begin{bmatrix} 2+iB & 2i-B & 2i+B & -2+iB \\ 3i-C & 3+iC & -3+iC & 3i+C \\ 2i+B* & -2+iB* & 2+iB* & 2i-B* \\ -3+iC* & 3i+C* & 3i-C* & 3+iC* \end{bmatrix}$$

Premultiplication with R^{-1}_{90xCH} gives the following expression for D(7)

$$\frac{1}{4}\begin{bmatrix} \begin{array}{l} 10+i(B+C \\ -B^*-C^*) \end{array} & \begin{array}{l} 2i-B+C \\ +B^*-C^* \end{array} & \begin{array}{l} B+C \\ +B^*+C^* \end{array} & \begin{array}{l} i(B-C \\ +B^*-C^*) \end{array} \\ \begin{array}{l} -2i+B-C \\ -B^*+C^* \end{array} & \begin{array}{l} 10+i(B+C \\ -F^*-C^*) \end{array} & \begin{array}{l} -i(B-C \\ +B^*-C^*) \end{array} & \begin{array}{l} B+C \\ +B^*+C^* \end{array} \\ \begin{array}{l} B+C \\ +B^*+C^* \end{array} & \begin{array}{l} i(B-C \\ +B^*-C^*) \end{array} & \begin{array}{l} 10-i(B+C \\ -B^*-C^*) \end{array} & \begin{array}{l} 2i+B-C \\ -B^*+C^* \end{array} \\ \begin{array}{l} -i(B-C \\ +B^*-C^*) \end{array} & \begin{array}{l} B+C \\ +B^*+C^* \end{array} & \begin{array}{l} -2i-B+C \\ +B^*-C^* \end{array} & \begin{array}{l} 10-i(B+C \\ -B^*-C^*) \end{array} \end{bmatrix} \tag{I11}$$

We follow now the evolution of the carbon single-quantum coherences.

$$d_{12}(7)=\frac{1}{4}(-2i-B+C+B^*-C^*)$$

$$d_{34}(7)=\frac{1}{4}(-2i+B-C-B^*+C^*)$$

$$d_{12}(7)+d_{34}(7)=-i \tag{I12}$$

The terms *B* and *C*, which contain the proton information, are absent from the sum. If we start the acquisition at *t*(7), with the decoupler on, we will not have a 2D. This is why Δ_2 still is necessary.

Proceeding as in (I.36) to (I.43) we have:

$$\begin{aligned} d_{12}(8) &= d_{12}(7)\exp(-i\Omega_C\Delta_2)\exp(-i\pi J\Delta_2) \\ &= -id_{12}(7)\exp(-i\Omega_C\Delta_2) \\ d_{34}(8) &= +id_{34}(7)\exp(-i\Omega_C\Delta_2) \end{aligned} \tag{I13}$$

Treating the detection as in (I.44) to (I.47) we obtain

$$d_{12}(9) = -id_{12}(7)\exp(-i\Omega_C\Delta_2)\exp(-i\Omega_C t_d)$$
$$d_{34}(9) = +id_{12}(7)\exp(-i\Omega_C\Delta_2)\exp(-i\Omega_C t_d) \qquad \text{(I14)}$$

$$M_{TC}(9) = M_{oC}\left[d_{12}^*(9) + d_{34}^*(9)\right]$$
$$= -iM_{oC}\left[d_{12}^*(7) - d_{34}^*(7)\right]\exp(i\Omega_C\Delta_2)\exp(i\Omega_C t_d)$$
$$= -i(M_{oC}/2)(B - B^* - C + C^*)\exp\left[i\Omega_C(t_d + \Delta_2)\right] \qquad \text{(I15)}$$

From (I10) we have

$$B - B^* = -2i\left(\cos\Omega_{13}t_e - i\sin\Omega_{13}t_e\right) - 2i\left(\cos\Omega_{13}t_e + i\sin\Omega_{13}t_e\right)$$
$$= -4i\cos\Omega_{13}t_e \qquad \text{(I16)}$$
$$C - C^* = -4i\cos\Omega_{24}t_e \qquad \text{(I17)}$$
$$M_{TC}(9) = -i(M_{oC}/2)(-4i\cos\Omega_{13}t_e + 4i\cos\Omega_{24}t_e)\exp\left[i\Omega_C(t_d + \Delta_2)\right]$$
$$= -2M_{oC}(\cos\Omega_{13}t_e - \cos\Omega_{24}t_e)\exp\left[i\Omega_C(t_d + \Delta_2)\right]$$

which confirms (I.51).

Fully coupled 2DHETCOR

If the proton decoupler is not turned on during the detection, the matrix elements d_{12} and d_{34} ,will evolve with different frequencies in the domain t_d. Each of them is proton modulated, even if their sum at time $t(7)$ is not, and this renders the delay Δ_2 unnecessary. The detection starts at $t(7)$ and we will have

$$M_{TC}(9) = -M_{oC}\left[d_{12}^*(7)\exp(i\Omega_{12}t_d) + d_{34}^*(7)\exp(i\Omega_{34}t_d)\right]$$

By introducing (I12), (I16), and (I17) in the expression above we obtain

$$M_{TC}(9) = -iM_{oC}\left(1/2 - \cos\Omega_{13}t_e + \cos\Omega_{24}t_e\right)\exp(i\Omega_{12}t_d)$$
$$-iM_{oC}\left(1/2 + \cos\Omega_{13}t_e - \cos\Omega_{24}t_e\right)\exp(i\Omega_{34}t_d)$$

which confirms (I.52).