

Figure A.3.7: Liquid Impulse Response Measurements for Run 14.8, N1-CEN, (3.6 MPa,  $U_G = 36 \text{ cm/s}$ ), Injection Time 22.4s

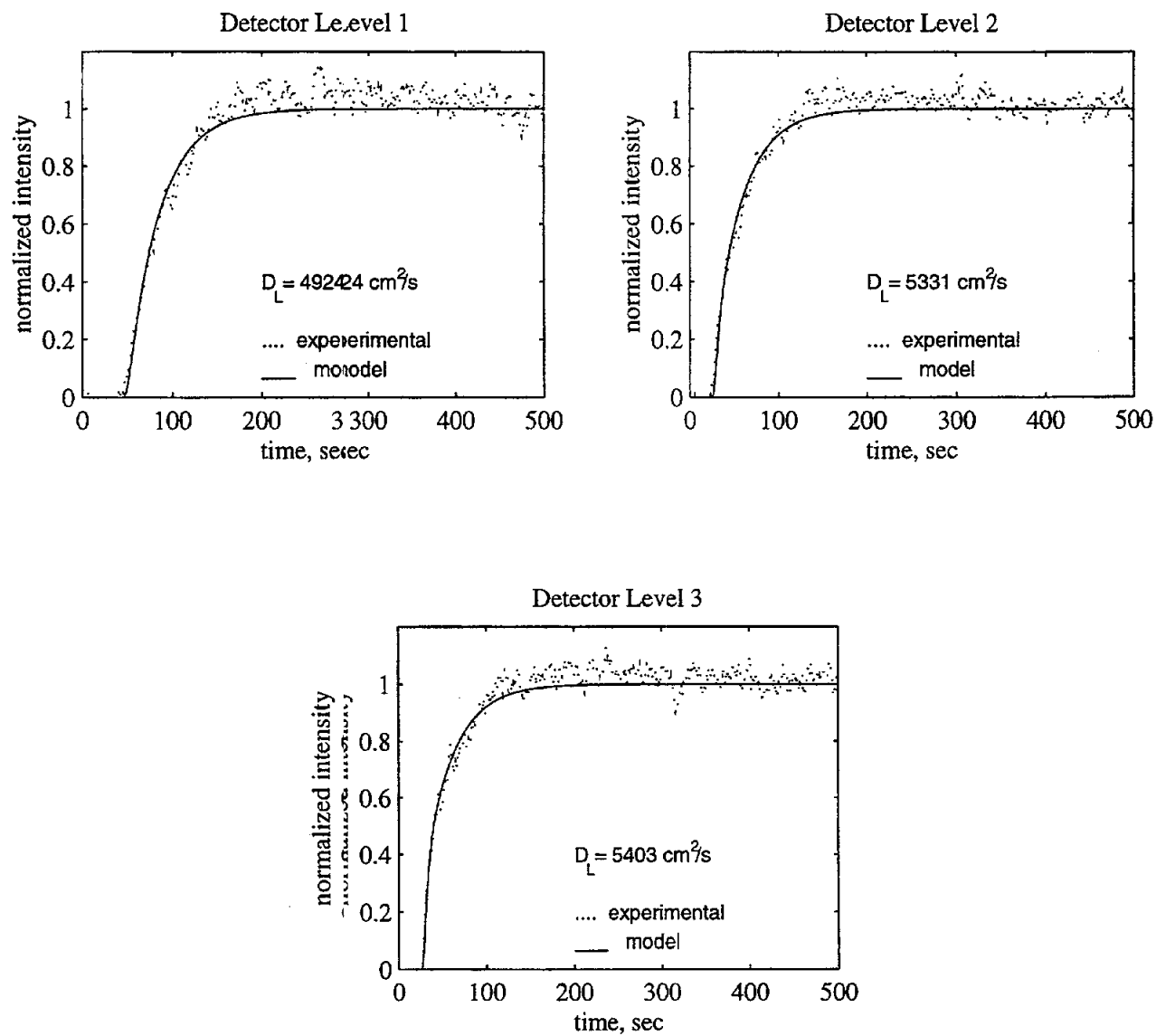


Figure A.3.8: Liquid Impulse Response Measurements for Run 14.8, N1-WALL, (3.6 MPa,  $U_G = 36 \text{ cm/s}$ ), Injection Time 39.6s

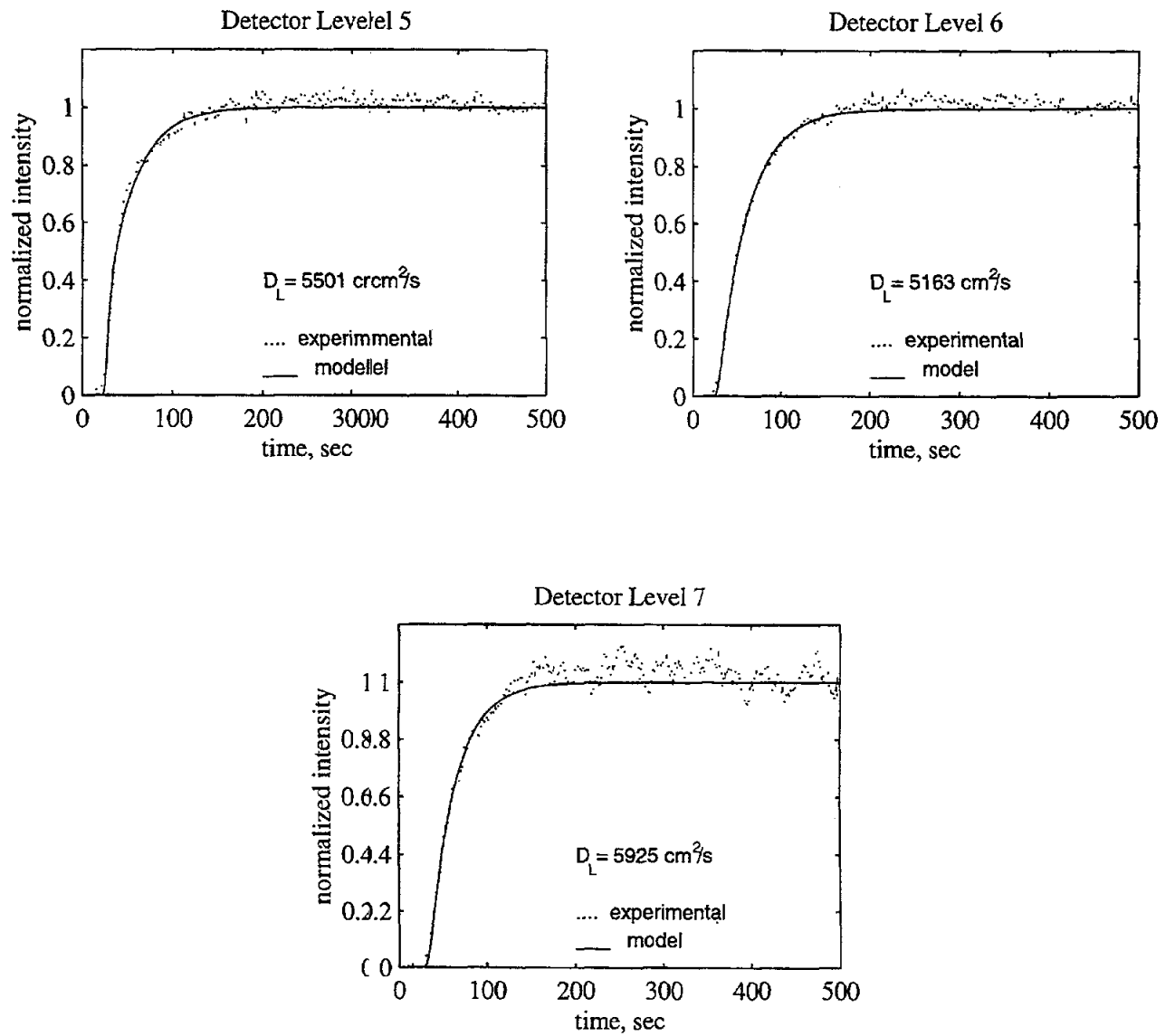


Figure A.3.8: Liquid Impulse Response Measurements for Run 14.8, N2-CEN, (3.6 MPa,  $U_G = 36 \text{ cm/s}$ ), Injection Time 20.8s

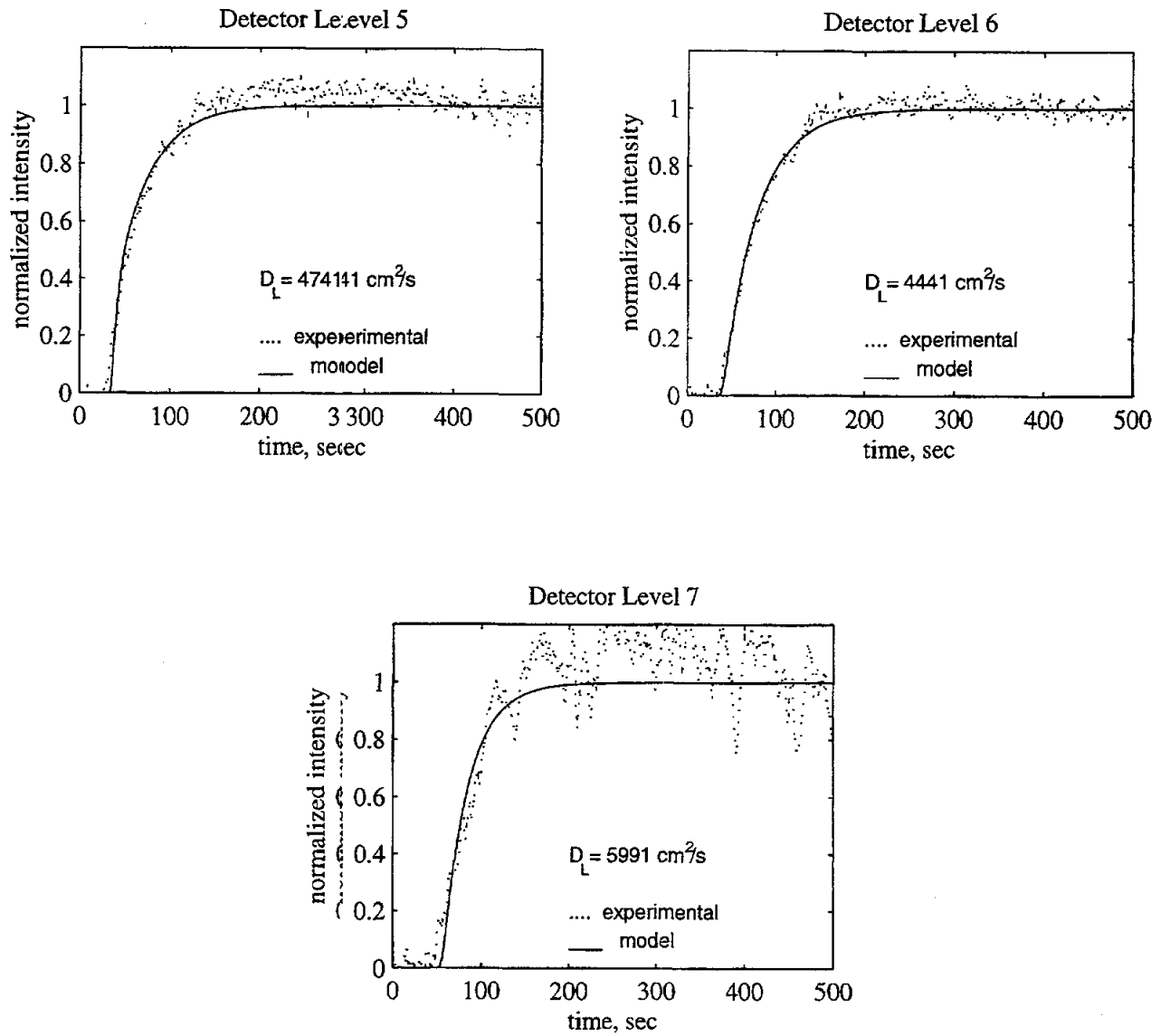


Figure A.3.10: Liquid Impulse Response Measurements for Run 14.8, N2-WALL, (3.6 MPa,  $U_G = 36 \text{ cm/s}$ ), Injection Time 39s

### 13 Appendix IW: Analysis of Variance (ANOVA)

This section discusses the statistical analysis of the model fitted parameters of the liquid and gas phase axial dispersion model using ANOVA (Box et al., 1978). We explain briefly the analysis for the liquid phase dispersion coefficients. The first test considered the data (liquid dispersion coefficients) obtained for a given process rate (run). For each process rate, four different injection points were used. The dispersion coefficients from each injection point were assumed to fall into a separate category or 'treatment'. In each treatment, the dispersion coefficients were obtained for measurements made at three detector levels. The data (dispersion coefficients) from within a treatment are assumed to differ due to random error. The objective is to find out if there are any real differences in the mean values associated with the different treatments. The FF statistic, or F ratio, defined as the ratio of the mean square error in the treatments ( $s_T^2$ ) to the mean square error between treatments ( $s_R^2$ ), was calculated.

$$FF = \frac{s_T^2}{s_R^2}; \quad s^2 = \frac{S}{n} \quad (31)$$

where  $S$  is the sum of square errors, and  $n$  is the degrees of freedom (size of sample - 1).

The data were tested using the null hypothesis, which states that the treatment means are equal. If the null hypothesis is true, this implies that the F ratio would follow an  $F$  distribution, which is defined as a distribution of the ratio of two variances obtained from two groups sampled from a normally distributed population. Each variance depends on the sample size or the degrees of freedom of each group.  $n_T$  and  $n_R$  are the degrees of freedom of the two groups for this analysis. The null hypothesis is verified by comparing the F ratio with the percentage points from a standard table of the  $F$  Distribution (Box et al., 1978) with  $n_T$  and  $n_R$  degrees of freedom and a certain significance level. In this case the significance level, which indicates the confidence level of the test, is set to be 10%. For 2 and 6 degrees of freedom the value from the  $F$  table is 3.46, and for 3 and 8 degrees of freedom, it is 2.92. An F ratio that is lower than the corresponding value from the  $F$  Table indicates that the null hypothesis is valid.

Table A.4.1. shows that the null hypothesis is rejected for runs 14.6 and 14.7, that is, the treatment means are different from each other, while for run 14.8, the hypothesis is accepted.

The analysis is then applied to the liquid dispersion data by considering all the data from a given run to belong to a single treatment. The means from the three runs, 14.6, 14.7 and 14.8, are compared as shown in Table A.4.2. Since the  $F$  ratio is much larger than the corresponding percentage point from the  $F$  Table, i.e., 2.49, the null hypothesis is rejected, which implies that the means of the three runs belong to different categories. Therefore there is a significant difference between the means of a certain process rate, which implies that there is a dependency of  $D_L$  on superficial gas velocity.

A similar analysis is performed for the gas phase model-fitted parameters. Two tracer experiments were conducted at each process rate. The parameters obtained from Case 1 were tested for the repeatability of the experiments at each process rate. The resulting  $F$  ratios for each of the parameters in Table A.4.3 show that except for  $D_G$  from Run 14.6, there is good repeatability of all the parameters at all process rates. As in the case of the liquid dispersion coefficients, an analysis of the effect of superficial gas velocity on the parameters (Table A.4.3 for Case 1 and Table A.4.4 for Case 6) shows that while the gas phase dispersion coefficients are dependent on gas velocity, both  $H$  and  $K_L a$  show no dependency.

Table A.4.1. ANOVA Table for Comparison of Mean Values within each Run

Run	Source of Variation	Sum of Squares (S)	Degrees of Freedom (n)	Mean Square ( $s^2$ )	Ratio $s_T^2/s_R^2$
14.6	Bet. Treatments (T)	11429238	2	5714619	4.69
	Within Treatments (R)	7358845	6	1226474	
14.7	T	3333876	3	1111291	5.13
	R	1733267	8	216658	
14.8	T	919538	3	306513	1.22
	R	251495	8	251495	

Table A.4.2. ANOVA Table for Comparison of Mean Values between Runs

Source of Variation	Sum of Squares (S)	Degrees of Freedom (n)	Mean Square ( $s^2$ )	Ratio $s_T^2/s_R^2$
Bet. Treatments (TT)	36609900	2	18304950	20.5
Within Treatments (R)	26790772	30	89302573	

Table A.4.3. ANOVA Table for Case 1

Parameter	I Run	Repeatability of Runs			Effect of $U_G$		
		mean	std. dev.	F	mean	std. dev.	F'
$D_G$ $cm^2/s$	144.6 - 1	6529	920	10.44	5637	1305	14.7
	144.6 - 2	4745	993				
	144.7 - 3	3041	1251	0.55	2801	1010	
	144.7 - 4	2561	974				
	144.8 - 5	4737	1068	0.22	4961	1504	
	144.8 - 6	5165	1032				
$K_{La}$ $1/s$	144.6 - 1	1.38	0.88	0.57	1.23	0.81	0.43
	144.6 - 2	1.03	0.76				
	144.7 - 3	0.91	0.58	0.001	0.907	0.92	
	144.7 - 4	0.90	1.25				
	144.8 - 5	1.125	0.94	1.37	1.18	0.97	
	144.8 - 6	1.25	0.89				
$H$	144.6 - 1	4.53	0.91	0.257	4.4	0.86	0.34
	144.6 - 2	4.27	0.88				
	144.7 - 3	4.18	0.70	0.20	4.33	1.08	
	144.7 - 4	4.48	1.42				
	144.8 - 5	3.61	0.59	1.23	4.04	1.32	
	144.8 - 6	4.48	1.82				

Table A.4.4. ANOVA Table for Case 6

Run	$D_G, cm^2/s$			$K_{La}, 1/s$		
	mean	std. dev.	F	mean	std. dev.	F
14.6	56499	1022		0.37	0.37	
14.7	29088	723	23.9	0.38	0.06	0.95
14.8	66221	1437		0.36	0.12	



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## 14 Appendix V:: Calculation of Henry's Law Constant

Vapor liquid equilibrium was calculated using suitable equations of state for the liquid and vapor phase, and considering the reactor conditions and composition of the outlet gas stream (more details regarding these calculations and the equations of state used will be provided by B. A. Toseland). The hydrocarbons used in the calculation were an estimate of the composition of the neutral oil phase in the reactor. From the VLE data, Henry's Law constant  $H$  for the tracer gas, argon, is obtained as :

$$H = \left( \frac{y_A}{x_A} \right) \quad (32)$$

where  $x_A$  is the mole fraction of argon in the liquid phase and  $y_A$  is the mole fraction of argon in the gas phase at equilibrium conditions.

For Runs 14.6 and 14.7 (press : 52 MPa and temp : 250 ° C),  $H = 5.86$ , and for Run 14.8 (press : 36 MPa and temp : 250 ° C),  $H = 8.11$ .

## 15 Appendix WI: Gas Phase Tracer Experiments and Model Fits

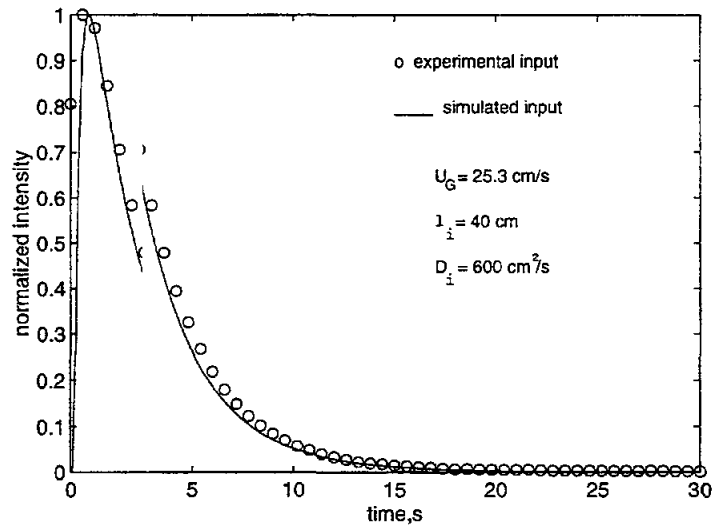


Figure A.6.1 (a): Simulation of Input Pulse to the Reactor, Run 14.6

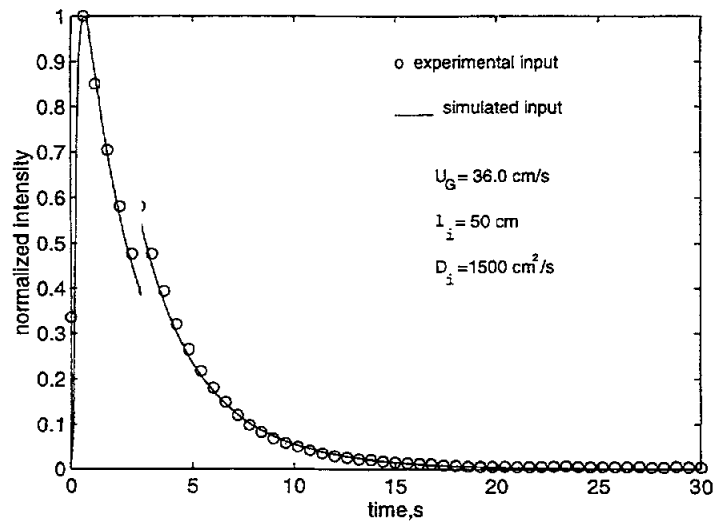


Figure A.6.1 (b): Simulation of Input Pulse to the Reactor, Run 14.8

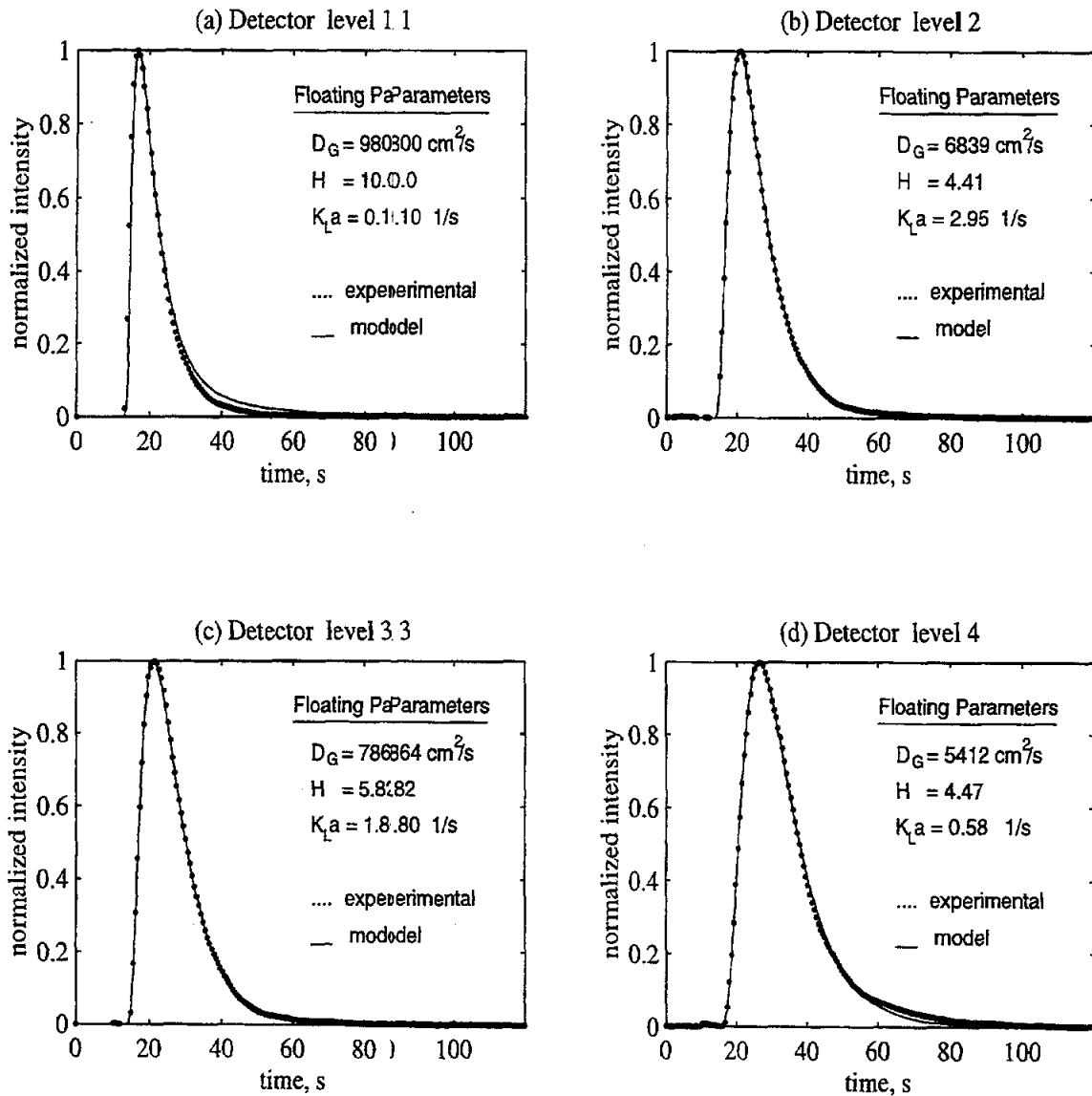


Figure A.6.2: Gas Phase Impulse Response for Case 1, Run 14.6 - 1, (5.2 MPa,  $U_G = 25 \text{ cm/s}$ ), Injection Time = 12.6s

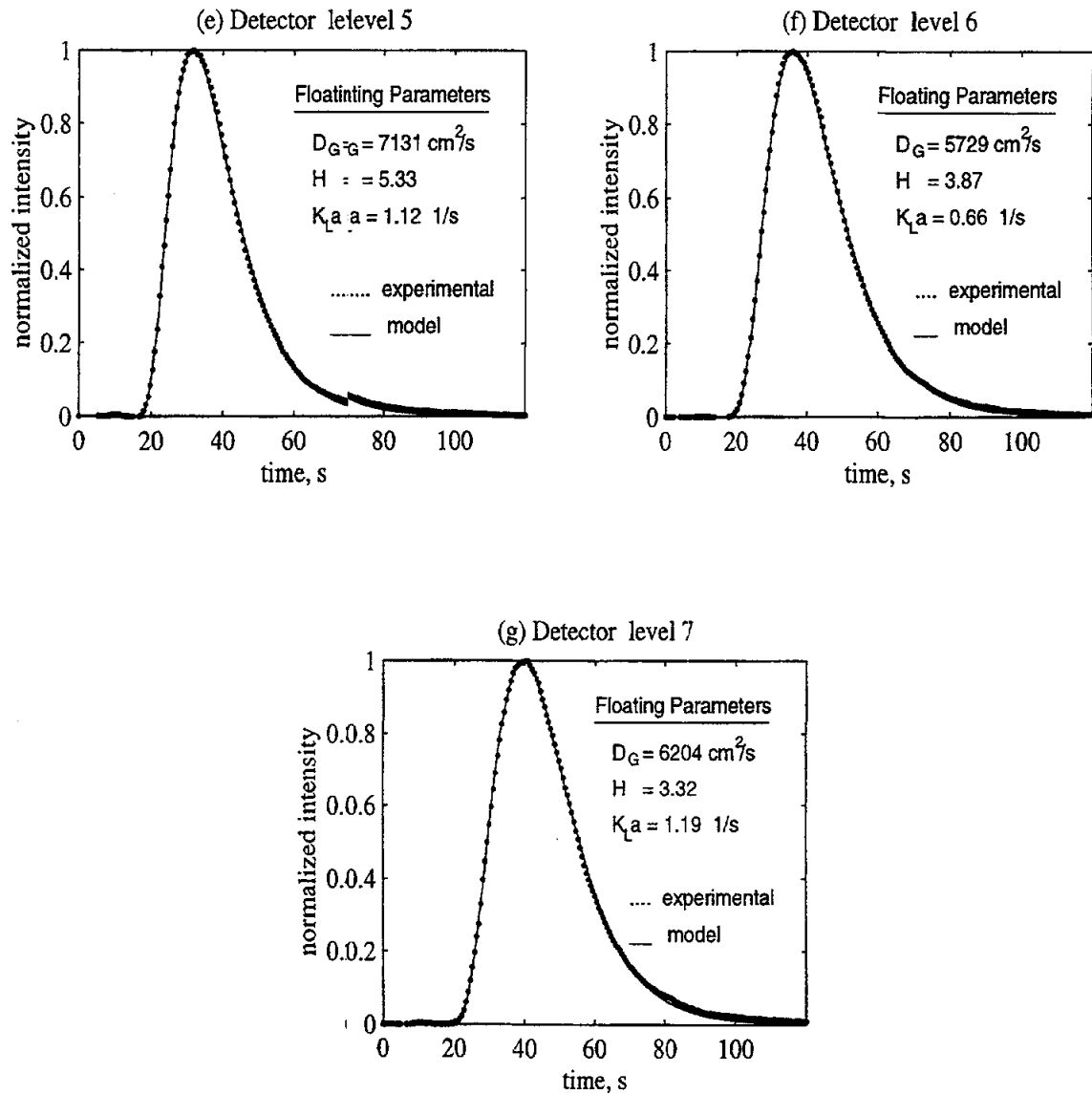


Figure A.6.2 (contd.): Gas Phase Impulse Response for Case 1, Run 14.6 - 1, (5.2 MPa,  $U_G = 25 \text{ cm/s}$ ), Injection Time 12.6s

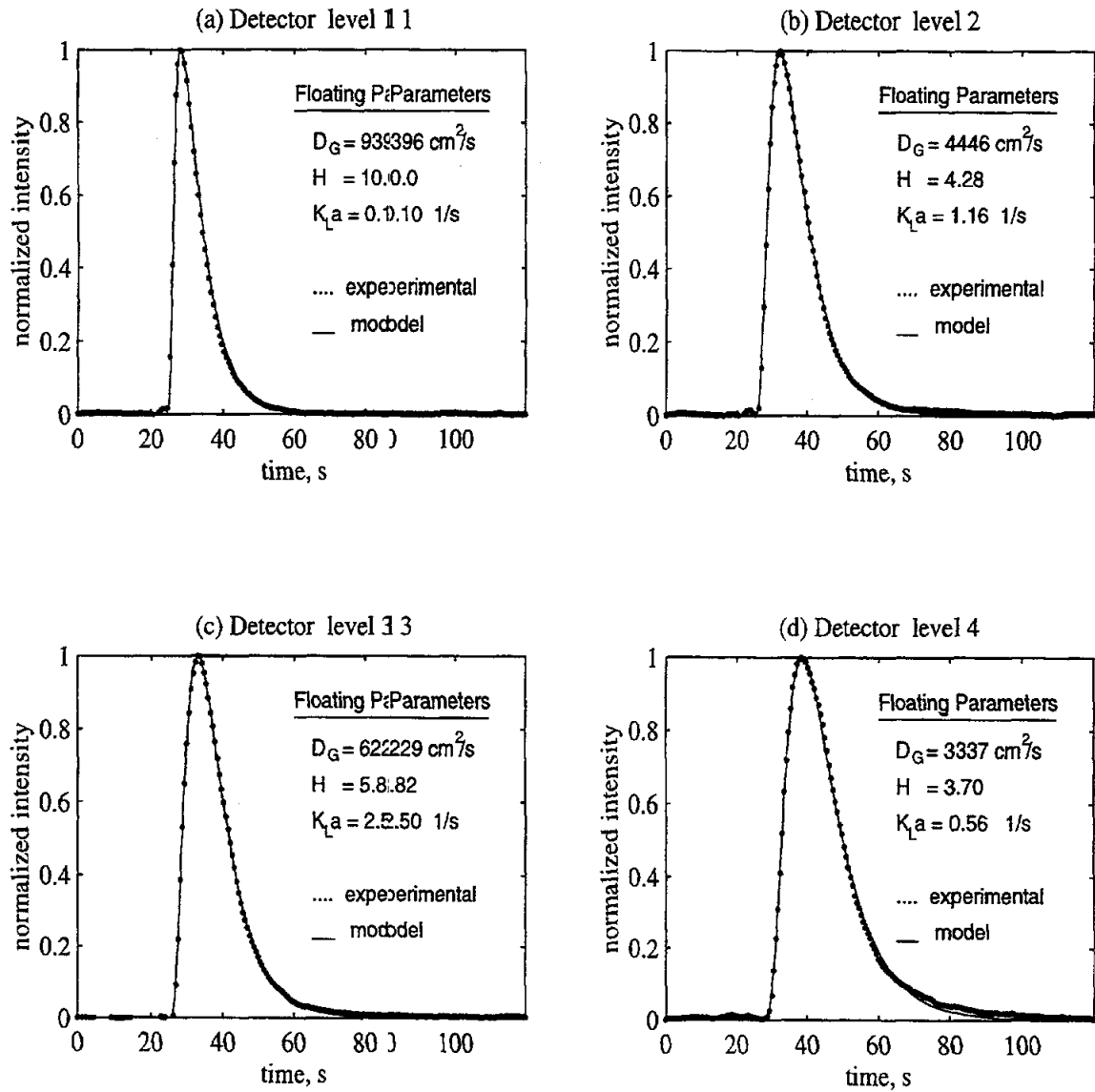


Figure A.6.3: Gas Phase Impulse Response for Case 1, Run 14.6 - 2, (5.2 MPa,  $U_G = 25 \text{ cm/s}$ ), Injection Time = 24s

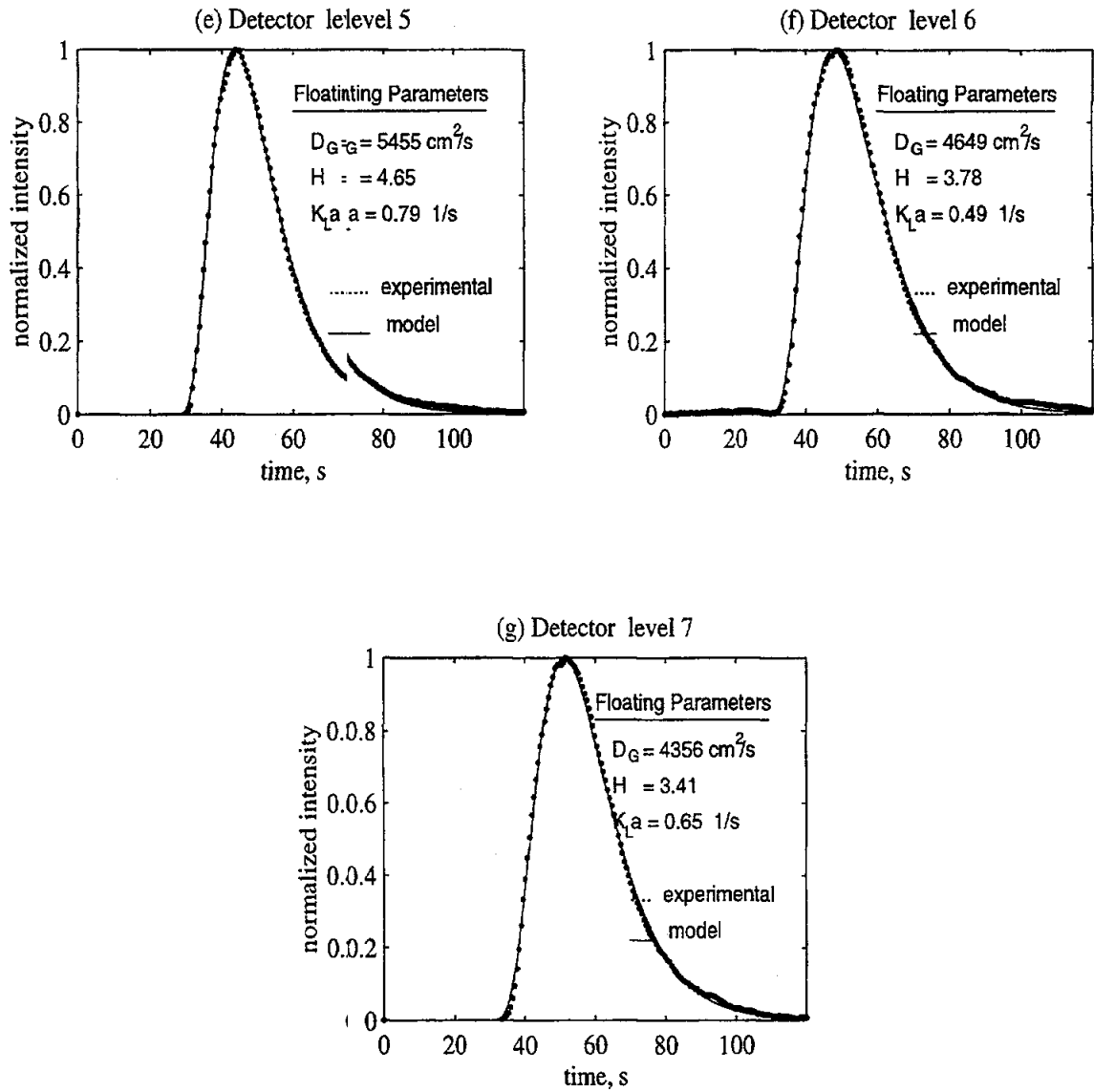


Figure A.6.3 (contd.): Gas Phase Impulse Response for **Case 1**, Run 14.6 - 2, (5.2 MPa,  $U_G = 25 \text{ cm/s}$ ), Injection Time 24s

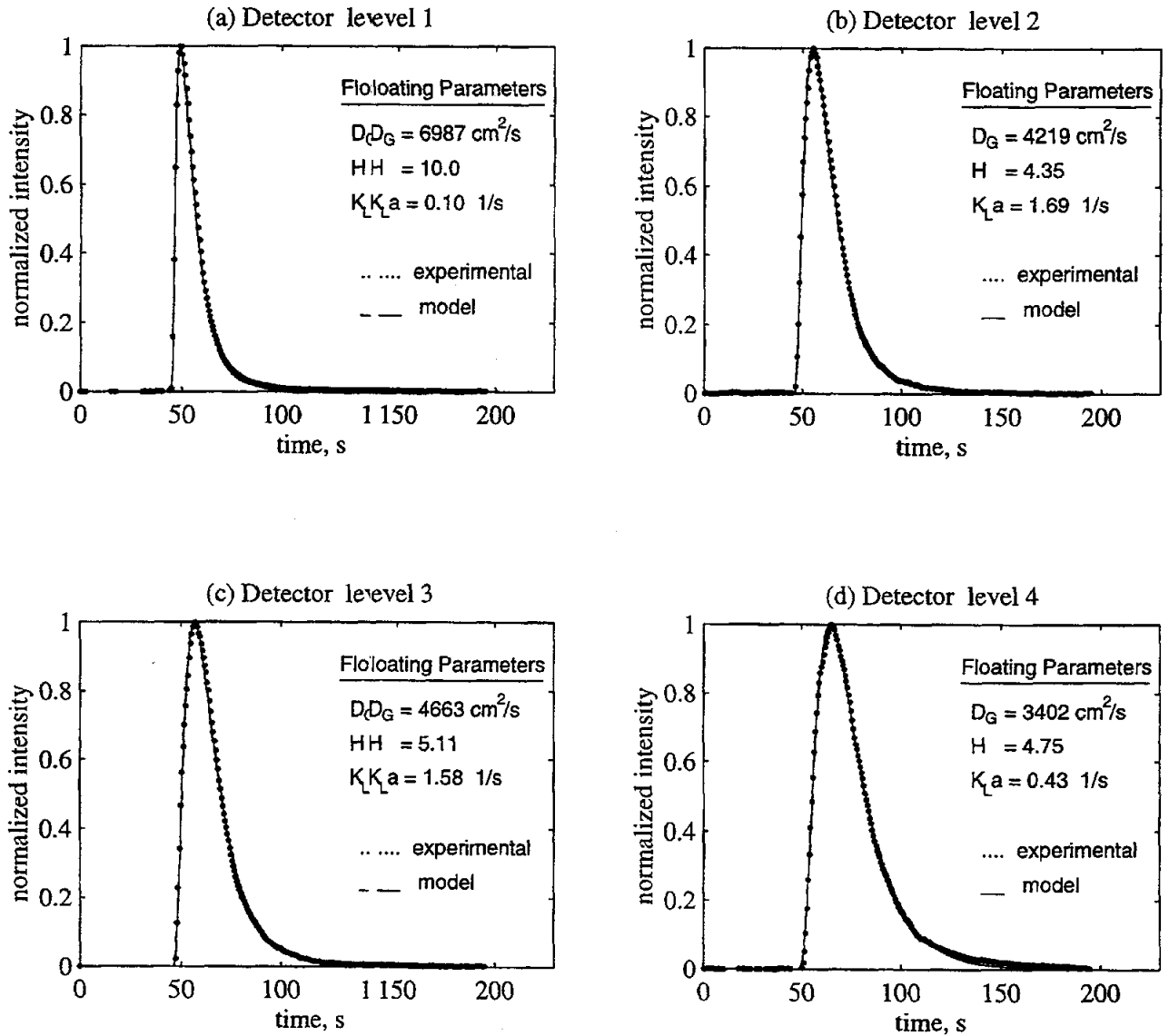


Figure A.6.4: Gas Phase Impulse Response for **Case 1**, Run 14.7 - 3, (5.2 MPa,  $U_G = 14 \text{ cm/s}$ ), Injection Time = 45s

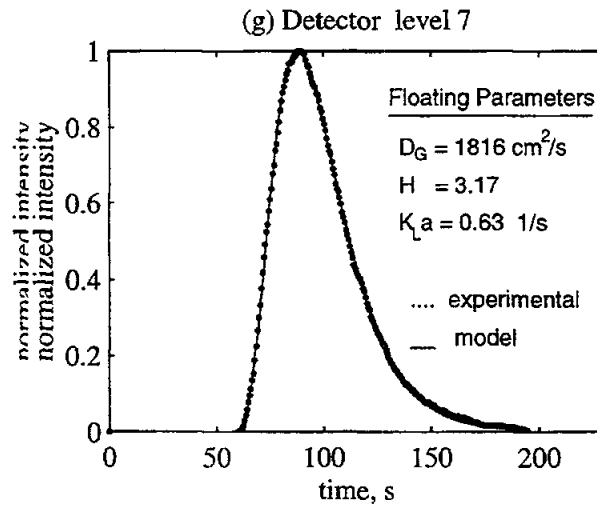
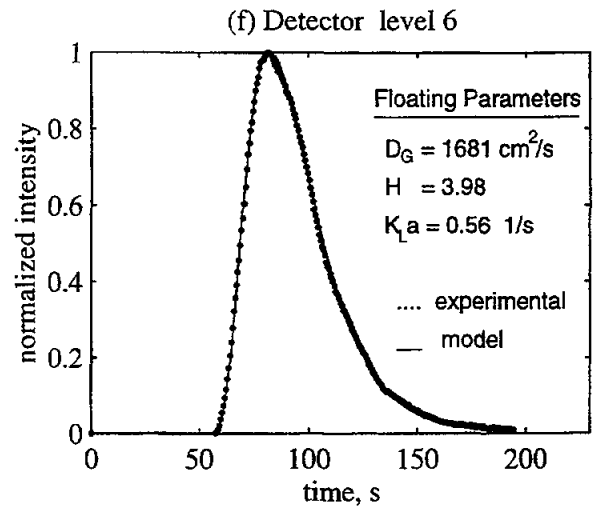
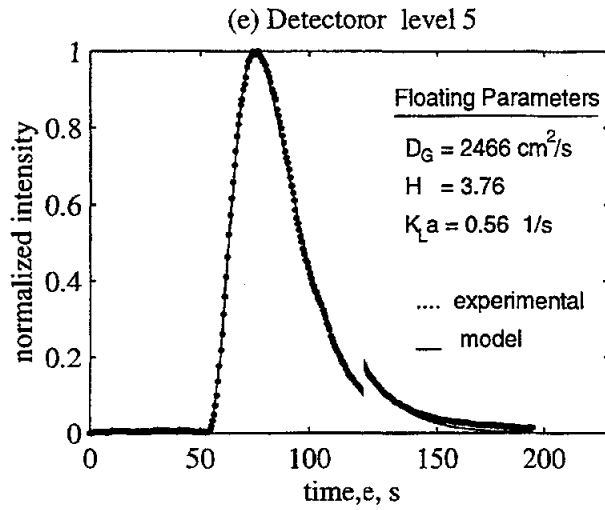


Figure A.6.4 (contd.): Gas Phase Impulse Response for Case 1, Run 14.7 - 3, (5.2 MPa,  $U_G = 14 \text{ cm/s}$ ), Injection Time 45s



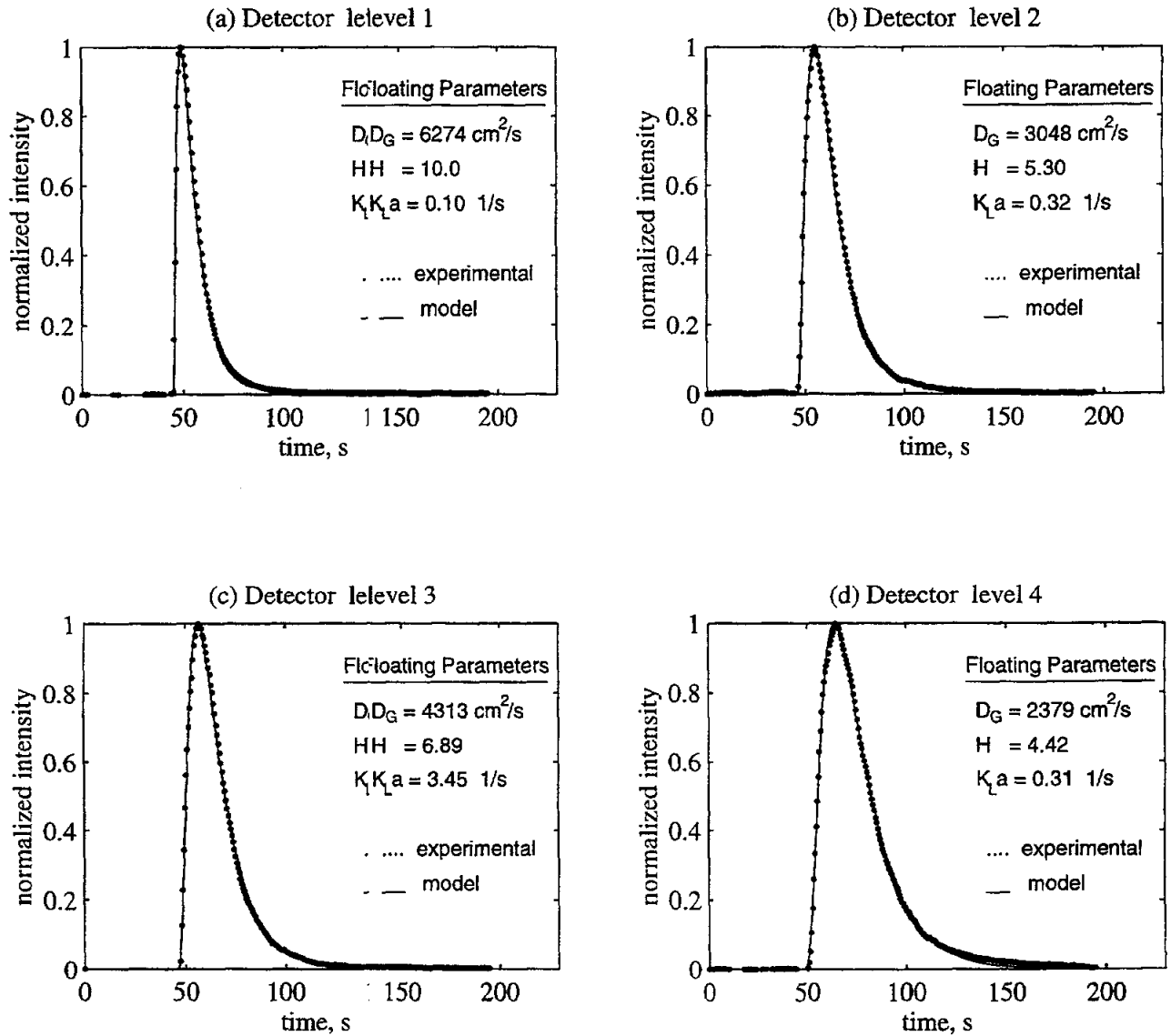


Figure A.6.5: Gas Phase Impulse Response for Case 1, Run 14.7 - 4, (5.2 MPa,  $U_G = 14 \text{ cm/s}$ ), Injection Time = 30.6s

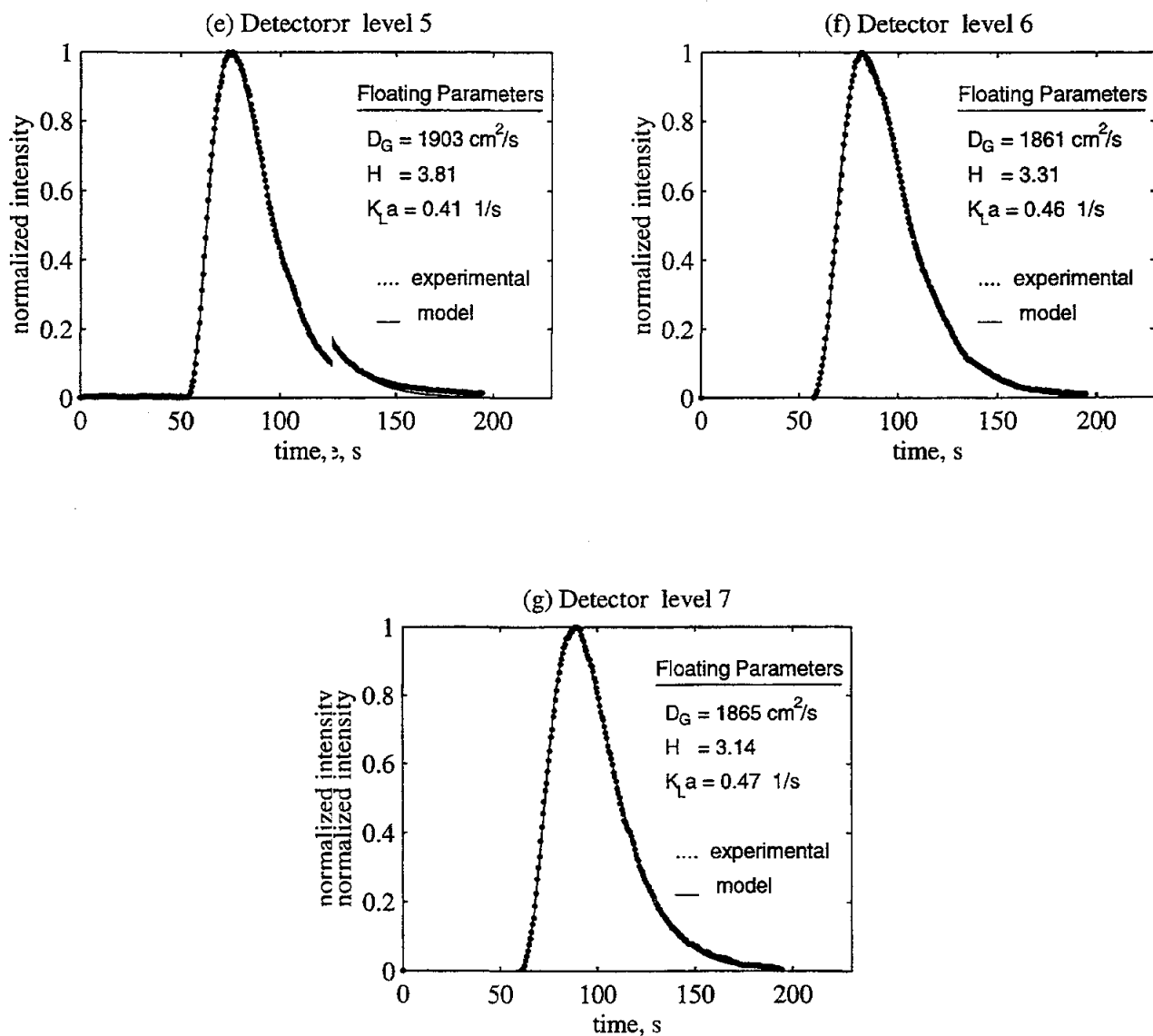


Figure A.6.6 (contd.): Gas s Phase Impulse Response for **Case 1**, Run 14.7 - 4, (5.2 MPa,  $U_G = 14 \text{ cm/s}$ ), Injection Time 30.6s

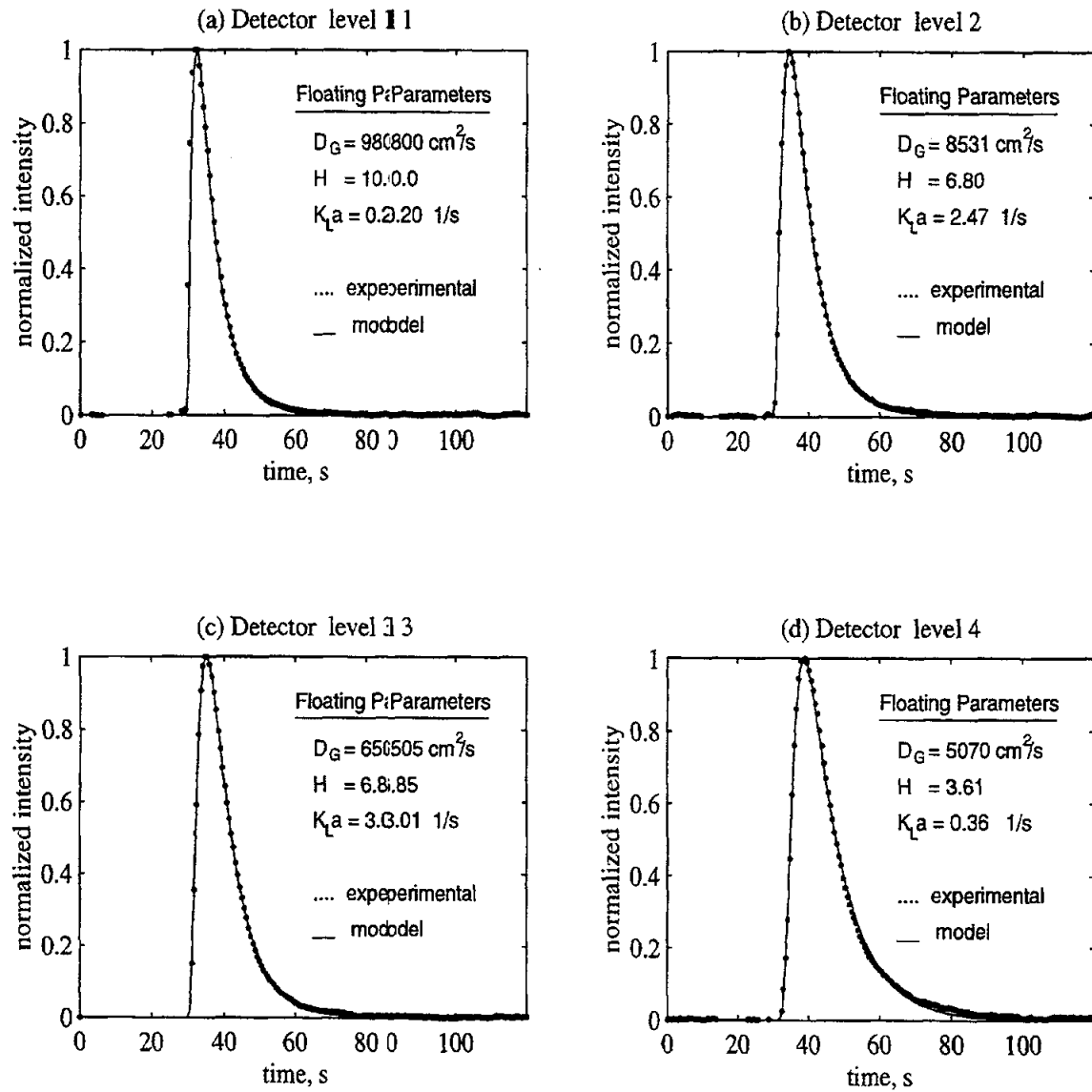


Figure A.6.6: Gas Phase Impulse Response for Case 1, Run 14.8 - 6, (3.6 MPa,  $U_G = 36 \text{ cm/s}$ ), Injection Time = 29.4s