Chapter 19

Error discussion

To calculate the error on the production rates for C_2H_2, C_2H_6 and C_3H_4 it is necessary to quantify and combine all uncertainties within the modeling process. The problem with a complex model as the one presented here is the large number of parameters. For a complete error discussion an error has to be derived for each parameter in the model. This would include all of the more than 1000 reactionrates used. However, even if for each of the parameter a separate error could be derived it would not be possible to calculate a formal error based on the laws of error propagation. This would require a complete and analytic knowledge of coupling between the different error sources.

To circumvent these problems a mixed approach was used. The main uncertainties have been identified and for each parameter the resulting errors are estimated by a parameter variation. The procedure is discussed for each set of parameters in the following sections. The difference in the resulting production rates of C_2H_2, C_2H_6 and C_3H_6 yields a good upper limit estimate for the resulting error. Table 19.6 summarizes all discussed sources of uncertainties and the maximal quantitative errors. Based on this data a combined error for the production rates can be estimated.

19.1   Nucleus abundance

The initial composition of the nucleus as an input parameter has been discussed in section 14. Unfortunately none of the assumed parent species have been observed at the same time as the observations used for this study. Section 14 describes in detail how the production rates for the heliocentric distances used in this study have been derived. Approximating the production rates introduces a certain degree of uncertainty. In the following paragraphs the effects of uncertainties for the main constituents of the coma are discussed separately.

A change in the production rate of one species yields also a change in the activity of the nucleus. This has an influence on the dynamics of the nucleus. A denser coma will transfer heat more efficiently and will reach the area of free molecular flow at larger heliocentric distances. However the effects are small for the range of uncertainties discussed here. The effects on the chemistry dominate. Therefore they are now discussed in detail.

19.1.1   Abundance of water

The water production rate was derived from a sublimation model by Huebner and Benkhoff [1999] and Benkhoff and Huebner [1995]. The model was scaled to the measurements by Weaver *et al.* [1999b]. The results have been compared to the post-perihelion measurements by Dello Russo *et al.* [2000]. The difference was generally small as can be see in Figure 14.2 in chapter 14 . To estimate the effect of the uncertainty in the water production on the production rates of C_2H_2, C_2H_6 and C_3H_4 the water production rate was increased and decreased by a factor of 2. Table 19.1 shows as an example the results for this test for the night Dec, 19. 1997.

$Q(H_2O)$	$Q(C_2H_2)$	$Q(C_2H_6)$	$Q(C_3H_4)$
	$[10^{25}\ s^{-1}]$		
2000.	63.7	91.1	53.3
3000.	66.7	96.2	54.7
4000.	**69.5**	**100.**	**55.8**
6000.	74.4	104.	56.9
8000.	76.1	109.	58.5

Table 19.1: Example for the sensitivity of C_2H_2, C_2H_6 and C_3H_4 production rates to uncertainties in the $Q(H_2O)$

The row printed in bold shows the nominal values, while the rows above and below represent an decreased and increased water production rate. An increase in the water production rate leads to a increase of the production rates for C_2H_2, C_2H_6 and C_3H_4 and vice versa. Looking at the formation chemistry as discussed in chapter 18 the reason for this behavior is found in the electron impact dissociation reactions. As has been discussed in section 12.1 water is most effective in cooling the electrons. An increased water production rate and thus a higher water density in the coma, leads to a more effective cooling of the electrons, and decreases the density of 'hot' electrons capable of dissociating C_2H_2 and C_3H_4 close to the nucleus. The production of C_2 and C_3 in this region is less effective. Decreasing the water production rate leads to a less effective cooling of the electrons, which puts the point at which the electron temperature increases at smaller nucleocentric distances (see section 12.1.2). The production of C_2 and C_3 by electron impact dissociation is in this case more effective. C_2 and C_3 are formed at smaller distances from the nucleus. A more effective production C_2 and C_3 yields a decrease in the derived production rates for C_2H_2, C_2H_6 and C_3H_4. The derived production rates of C_2H_2, C_2H_6 and C_3H_4 increase if the C_2 and C_3 production is less effective. The shape of the profiles are affected as well, but the effects are small.

The same test has been repeated for various heliocentric distances to quantify the effect of uncertainties on the water production rates. An uncertainty of a factor of 2 on the water production rates has a net effect on the production rates for C_2H_2 and C_2H_6 of about 10% and for C_3H_4 of about 5% (see also table 19.6).

19.1.2 Abundance of CO and CO_2

The CO production rates have been adopted from the measurements by Biver *et al.* [1997]. The values have been interpolated to the heliocentric distances needed for this study. Based on the errors given by Biver *et al.* [1997] the uncertainty on the production rate is less than 50 %. Therefore to study the effect on the results obtained with the ComChem model, the same model was computed with a nucleus depleted by 50 % in CO and enriched by 50% in CO. An example of the results for the night of Dec. 19, 1997 is shown in table 19.2. Again this test has been repeated for a number of different nights. The effect on the production rates for $Q(C_2H_2)$, $Q(C_2H_6)$ are within 20% and the effect on $Q(C_3H_4)$ is within 10% (see table 19.6). CO is one of the sources for electrons in the coma. Therefore a variation in the CO abundance affects electron impact dissociation reactions. A higher CO abundance yields an increased production of electrons which then can produce more C_2 and C_3 by electron impact dissociation.

Q(CO)	$Q(C_2H_2)$	$Q(C_2H_6)$	$Q(C_3H_4)$
		$[10^{25}\ s^{-1}]$	
4035.	80.2	118.	59.8
6050.	74.4	108.	57.6
8070.	**69.5**	**100.**	**55.8**
10087.	64.3	92.1	54.4
12100.	57.9	83.3	51.5

Table 19.2: Example for the sensitivity of C_2H_2, C_2H_6 and C_3H_4 production rates to uncertainties in the Q(CO)

For the CO_2 production rates the same variation was assumed as for the CO productionrate. Table 19.3 shows again the results for the night of Dec. 19, 1997. The effect on the production rates for $Q(C_2H_2)$, $Q(C_2H_6)$ are within 20% and the effect on $Q(C_3H_4)$ is within 10% (see table 19.6). CO_2 is the second most important source of electrons as it is a source for CO. For this reason varying the abundance of CO_2 in the initial composition has basically the same effect as varying the CO abundance.

$Q(CO_2)$	$Q(C_2H_2)$	$Q(C_2H_6)$	$Q(C_3H_4)$
		$[10^{25}\ s^{-1}]$	
1360.	80.1	118.	58.7
2040.	73.2	107.	56.2
2720.	**69.5**	**100.**	**55.8**
3400.	64.8	92.9	54.9
4080.	58.5	84.9	52.8

Table 19.3: Example for the sensitivity of C_2H_2, C_2H_6 and C_3H_4 production rates to uncertainties in the $Q(CO_2)$

19.1.3   Abundance of minor species

The minor species have hardly any effect on the chemistry for the formation of C_2 and C_3. Based on the discussion in section 18 and the history plots in appendix D the reactions involving minor species are several magnitudes less important than the main reactions. They are included mainly for completeness. For test purposes the abundance of several minor species (CH_3OH, CH_4, CH_3CN, NH_2CH_3)have been varied by an order of magnitude. The effect on the production rates of C_2H_2, C_2H_6 and C_3H_4 was smaller than the 5 % margin allowed for the fitting of the profile (see also table 19.6).

19.2   Reaction rates

The reaction rates for the chemistry part of the ComChem model are the parameters with the largest uncertainties. Furthermore due to the complexity of the reaction network classical error calculation methods are not applicable. Ideally the reaction network would include a mechanism for error tracking. Error tracking would allow to give the reaction rates with their uncertainties and the code itself would calculate errors based on these uncertainties and would track the accumulating errors on each species. While such procedure exist in principle they are not yet included in the ComChem model.

To get a quantitative estimate of the errors produced by uncertainties in the most important reactions (as identified in section 18) a similar approach as for the production rates was used. Each critical reaction was studied separately. The reaction rate has been set to the smallest and to the largest likely value and the model has been used with these rates. The differences in the results for $Q(C_2H_2)$, $Q(C_2H_6)$ and $Q(C_3H_4)$ give an estimate for the maximal error caused by the uncertainties in the reaction rates. The derived values for the errors associated with the variation of each of the reaction rates are listed in table 19.6.

At the same time studying the changes in the chemistry for the three cases (minimal, nominal and maximal reaction rate) allows to determine the qualitative effect of the uncertainty. Of special importance here are possible changes of the main reaction pathways which have be determined in section 18.

19.2.1   Optical depths effects

For a realistic quantitative model of coma chemistry opacity calculations are important. These affect all reaction rates in relation to photo chemistry. In the far-ultraviolet, the Sun can be essentially invisible from the surface of an active nucleus. The effects of opacity, in general, are a delay of the production of the daughter species, a reduction in their peak number density, and a change in the shape of their radial profile in the coma. However, although the chemistry is delayed by the coma's opacity, it is not stopped. Giguere and Huebner [1978] showed that ultraviolet opacity reduces the total production of daughter and grand-daughter species over the entire coma volume only by less than a factor of 2. The effect is mainly observable near the nucleus at distances far less than 10000 km. Even a high optical opacity has little or no effect on the shape of the radial profile for distances

greater than 10000 km from the nucleus. These calculations were done for a Halley-type comet at 1 AU. Since all models in this work are performed for heliocentric distances greater than 2.5 AU, it might be assumed, that the effects of opacity are even smaller. One has to be careful though, because the activity of comet Hale-Bopp at 2.5 AU was much higher than the activity of a Halley-type comet at this heliocentric distance. However Combi [2002] calculated for comet Hale-Bopp at 1 AU heliocentric distance that the coma is optical thick only up to 500 - 1000 km from the nucleus. Therefore even for the highly active comet Hale-Bopp at heliocentric distances greater 3 AU an optical thin coma can be assumed and thus opacity can be neglected.

19.2.2 Photodissociation rate coefficients

The photodissociation rate coefficients may be uncertain for several reasons. First, many values may be systematically underestimated because the input cross sections have been measured and/or theoretically calculated only for a limited range of wavelengths. Extrapolation of these cross sections may introduce errors in the calculations of the photodissociation rates. A second source of uncertainty is the unknown temperature-dependence of cross-section values. Wu *et al.* [1989] demonstrated the importance of this issue for hydrocarbon species when they found that the C_2H_2 cross sections at 155K could vary by as much as 40% from the values at 295K , a typical temperature for the measurements which supply the majority of the cross-sections data used in this work. Finally, and most importantly, a significant source of uncertainty in calculating the photodissociation rate coefficients for the reactions in table 14.3 is the lack of available detailed information on the branching ratios (probabilities of producing a particular set of products upon absorbing a photon) as a function of wavelength. There are often large variations in measured branching ratios for a particular reaction at different wavelengths (for example see Yung *et al.* [1984]).

Another uncertainty can arise from the numerical approach used to calculate the reaction rates. As has been discussed in section 12.2 reaction rates are derived using equation (4.3). Neither the solar flux nor the cross section can be given as an analytic expression. Therefore the integral has to be solved numerically and the results depend on the integration method used and on the quantization of the solar flux and cross section. Furthermore there is no standard solar flux. The solar flux used by different authors can vary. A comparison of the reaction rate for the reaction $C_2H_4 + h\nu \longrightarrow C_2H_2 + H_2$ derived by Moses [2000] to be $14.8 \cdot 10^{-6} s^{-1}$ and by Huebner *et al.* [1992] to be $26.3 \cdot 10^{-6} s^{-1}$ showed a difference of approximately 40 % although the same literature sources for the cross sections have been used.

For the photodissociation reactions of C_2H_2 an uncertainty of a factor of 5 was assumed. This includes the effect of temperature dependence discussed above, as well as uncertainties in the branching ratios and numerical uncertainties. The main effect is to steepen the profile of C_2, if the reaction rates are increased and vice versa to flatten it if the reaction rates are decreased. While this generally leads to a decrease in the fit quality it also has a slight effect on the production rates for C_2H_2 and C_2H_6. An increased reaction rate for the direct photodissociation of C_2H_2 forming C_2 leads to a slight decrease in the derived C_2H_2 and C_2H_6

production rate. The same effect, but to a much smaller degree is found for the reaction $C_2H_2 + h\nu \longrightarrow C_2H + H$. Decreasing the reaction rates has the opposite effects. The variation of the reactionrate for the photodissociation of C_2H_2 by a factor of 5 has a total effect on the production rates for C_2H_2 and C_2H_6 of about 10% (see also table 19.6)

For the photodissociation of C_2H, again an uncertainty of a factor of 5 was assumed following the same argumentation as for the photodissociation of C_2H_2. The effects are basically the same, although not as pronounced as for C_2H_2. The reason here are the two competing processes forming C_2, one by direct photodissociation of C_2H_2, the other via C_2H. While a change in the reaction rates for C_2H_2 affects both channels, a change in the reaction rates for C_2H affects only one channel. The effects on the production rates for C_2H_2 and C_2H_6 are smaller than the effects caused by changes in the C_2H_2 reaction rates. The total effect on the production rates for C_2H_2 and C_2H_6 is about 5% (see also table 19.6).

The photodissociation rates for C_3H_2 and C_3 have been derived in this work. The procedure is described in details in paragraph 14.2.2. The errors based on this determination are only ≈ 5 %. However the error is only derived from the standard deviation of the minimization routine and is underestimating the real error. It is valid to assume that the uncertainties on these two reaction rates are at least of the same order as for the just discussed photodissociation of C_2H_2 and C_2H. Therefore to test the sensitivity of the resulting production rate for C_3H_4 the reaction rates have been varied by a factor of 5.

Increasing the C_3H_2 photodissociation rates steepens the C_3 profile, because the molecule is destroyed closer to the nucleus. The effect of an increased C_3 photodissociation rate is to flatten out the profile. This affects the derived C_3H_4 production rate, especially the variation of the C_3 photodissociation rate. An increase in this reaction rate leads to an increase in the derived C_3H_4 productionrate. The reason is that a higher dissociation rate of C_3 means that more of the radical is destroyed close to the nucleus. In order to reproduce the observed densities in the spatial profile the abundance of the parent has to be increased. The variation of the reactionrates for the photodissociation of C_3H_2 and C_3 has total effect on the productionrate of C_3H_4 of about 30% each (see also table 19.6).

19.2.3   Electron impact dissociation rate coefficients

Very little laboratory work is done on the cross sections for electron impact dissociation of hydrocarbons as discussed in sections 11.1 and 11.2.

For the electron impact dissociation of C_2H_2 the reaction rate coefficients derived by different methods can differ up to a factor of 10 for some temperature regions.

In order to test the sensitivity to the uncertainties the reaction rates for the direct formation of C_2 by electron impact dissociation of C_2H_2 the rate has been varied by a factor of 10. As an example Figure 19.1 shows the plot for the night of Dec 19, 1997. An increased reaction rate leads to a higher efficiency of this formation process of C_2. This steepens the profile slightly but the effect is small compared to the errors on the profile. A decreased reaction rate flattens the profile slightly. The resulting differences for the production rates of C_2H_2 and C_2H_6 as listed in table 19.6 are larger than the errors due to the uncertainty in the photodissociation of C_2H_2. The reason for this is the higher uncertainty assumed for the

electron impact dissociation reaction compared to the uncertainty for the photodissociation rate.
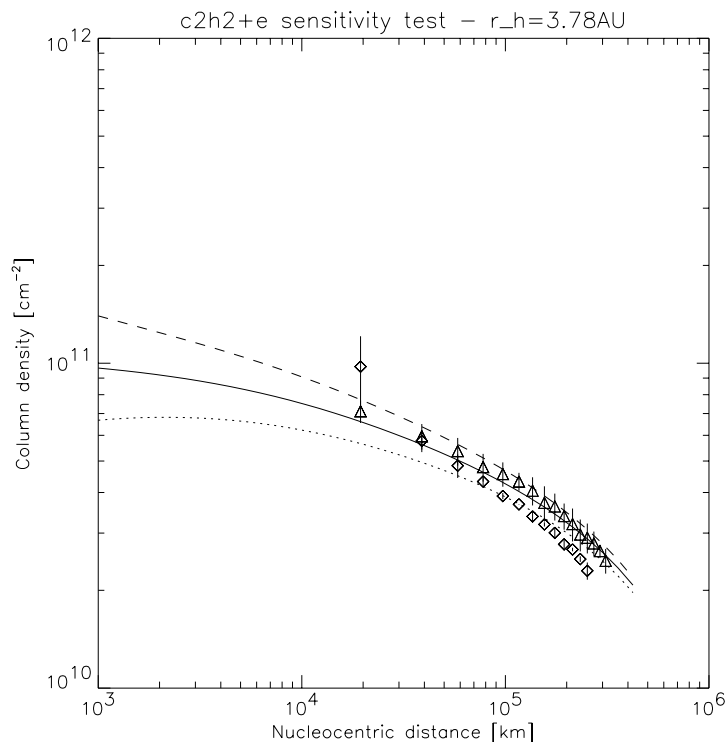

Figure 19.1: Example for sensitivity test for electron impact dissociation of C_2H_2 (solid line: nominal value, dotted line: reaction rate decreased by a factor of 10, dashed line: reaction rate increased by a factor of 10)

The same test was performed for the electron impact dissociation of C_2H_2 forming C_2H. For the reaction rate an uncertainty of a factor of 10 was assumed, following a similar argumentation as above. Again the profile steepens if the reaction rate is increased. The effect is even smaller than for the electron impact dissociation of C_2H_2 forming C_2. This is caused by the competing reactions forming C_2H. Consequently the effects on the production rates of C_2H_2 and C_2H_6 are slightly smaller than for the direct electron impact dissociation of C_2H_2.

For the electron impact dissociation of C_3H_4 the situation is more difficult. The dissociation of C_3H_4 by electron impact is unlikely to be a single step process forming C_3 directly. The reaction rate used in this work was derived by Keady and Huebner (published in Schmidt *et al.* [1988] and in Boice *et al.* [1986]). It is the value for the total destruction rate of C_3H_4 by electron impact dissociation based on theoretical calculations. Since the branching ratios and the details of the subsequent reactions are unknown this is the only value which can be calculated. The uncertainty on this total rate can be estimated to be of an order of magnitude (Personal communication with Keady [2001]).

Using the same method as before the reaction rate for the electron impact dissociation of
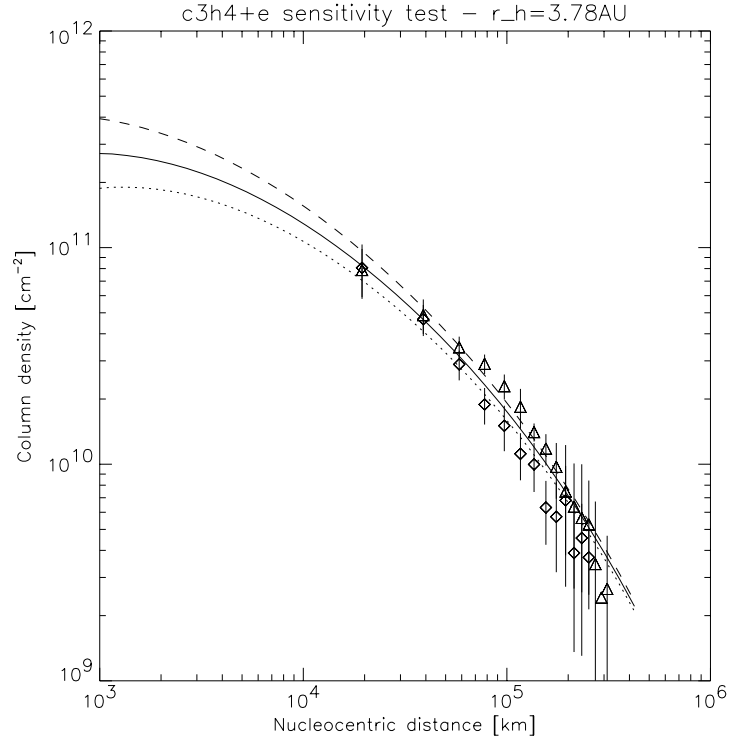
Figure 19.2: Example for sensitivity test for electron impact dissociation of C_3H_4 (solid line: nominal value, dotted line: reaction rate decreased, dashed line: reaction rate increased)

C_3H_4 has been varied by a factor of 10. The effect on the resulting production rates of C_3H_4 can be up to 50 %. An increased reaction rate leads to a fast destruction of C_3H_4 yielding a steeper C_3 profile. In order to match the observed C_3 spatial profile the C_3H_4 abundance has to be increased. Decreasing the reaction rates has as expected the opposite effect. The net effect on the derived productionrate of C_3H_4 is about 50% (see table 19.6).

19.2.4   Main reaction pathways

During all parameter variations for the different reaction types the influence on the relative importance of the reaction has been checked. However even the variation by an order of magnitude for the electron impact dissociation rates does not change the reaction network as defined in 18 drastically. Photodissociation and electron impact dissociation are by far the dominant processes in the formation of C_2 and C_3. Changing the reaction rates can shift the relative importance of the these two reaction types, but there have been no cases where a different reaction class became dominant.

19.3 Convergence

The determination of the production rates for C_2H_2, C_2H_6 and C_3H_4 relies on iteration methods. For these methods it is important to guarantee that the iteration converges on the same result independent of the starting values.

The convergence was checked routinely while analyzing the data. For several data points the iterations have been repeated with different starting values, always yielding the same results within a 5 % margin. An example for this testing is shown in table 19.4. This example is related to the example used in **Step 2** of section 15. The upper block shows the iteration as performed originally. The next three blocks shows iteration performed using different starting values. Independent of the starting values the iterations converge quickly to a value within the 5 % margin. The last column lists the derived production rates for C_3H_4. The differences between the iterations are smaller then 5 %.

Iteration	k	A(C_3H_4)	Q(C_3H_4) [s^{-1}]
0	0.1963	**0.086884**	$34.800 \cdot 10^{26}$
1	0.7899	0.017055	$6.8211 \cdot 10^{26}$
2	0.9841	**0.013472**	$5.3888 \cdot 10^{26}$
0	0.1022	**0.160553**	$64.200 \cdot 10^{26}$
1	0.8211	0.016409	$6.5628 \cdot 10^{26}$
2	0.9840	**0.013473**	$5.3887 \cdot 10^{26}$
0	0.7811	**0.018409**	$7.3600 \cdot 10^{26}$
1	0.8941	0.014379	$5.7515 \cdot 10^{26}$
2	1.0312	**0.012856**	$5.1424 \cdot 10^{26}$
0	1.6951	**0.007534**	$3.0000 \cdot 10^{26}$
1	1.0381	**0.012771**	$5.1084 \cdot 10^{26}$

Table 19.4: Iterations for C_3H_4 abundance using different starting values

19.4 Fit to the profile

The modeled spatial profiles have been fitted to the observed profiles with a deviation of not more than 5%. This is well below the typical errors on the spatial profiles. For some iterations modeled spatial profiles have been fitted with an even smaller maximal deviation. The effect of the maximal deviation on the resulting production rates has been tested. In order to do so the modeled profiles have been fitted to 0.95, 1.0 and 1.05 times the observed spatial profile. The resulting difference in the production rate was less than 5 % for all cases. For the night of Jan. 20, 1998 the two spatial directions have been fitted separately. This night showed an unusually high asymmetry. The resulting difference on the production rates are listed in table 19.5.

	$Q(C_2H_2)$	$Q(C_2H_6)$ $[10^{25}\ s^{-1}]$	$Q(C_3H_4)$
sunward	90.4	183.	132.4
tailward	73.3	146.	91.5
Difference	$\sim 20\ \%$	$\sim 20\ \%$	$\sim 40\ \%$

Table 19.5: Productionrates derived from asymmetric spatial profiles obtained on the night of Jan. 20, 1998

The asymmetry has the largest effect on the production rate of C_3H_4, the production rates of C_2H_2 and C_2H_6 are affected to a lesser extent.

All other nights show little or no significant asymmetries in the profiles for the two spatial directions. Therefore this effect is not included in the quantitative error estimated below.

19.5   Estimating the quantitative errors

To compute the final errors associated with the production rate for each of the observations, it is necessary to combine the estimates for the quantitative errors as listed in table 19.6. As has been stated, these errors are realistic upper limits for the effect of each uncertainty. The total error is a combination of each of these error terms. Because the errors are not independent the laws of error propagation are not valid here.

For $Q(C_2H_2)$ and $Q(C_2H_6)$ the combined error can be estimated to be $\approx 30\%$, while for $Q(C_3H_4)$ an error of $\approx 50\ \%$ can be estimated. These estimates are based on a weighted average of the errors as listed in table 19.6. The validity of these estimates has been tested by changing several parameters at the same time. The accumulative error was for all cases within the given estimates.

To derive meaningful errors the principle errors derived in this section are combined using the law of error propagation with the errors derived from the fitting procedure as described in section 15. The use of the law of error propagation is valid here because these two types of errors are strictly independent. The resulting error are shown in table 17.1 in chapter 17.

Variation of	varied by a factor of	Upper limit for the quantitative error		
		$Q(C_2H_2)$	$Q(C_2H_6)$	$Q(C_3H_4)$
Abundance of H_2O	2	10%	10%	5%
Abundance of CO and CO_2	50%	20%	20%	10%
Abundance of minor species	10	5%	5%	5%
$C_2H_2 + h\nu \longrightarrow C_2 + H_2$	5	10%	10%	
$C_2H_2 + h\nu \longrightarrow C_2H + H$	5	5%	5%	
$C_2H + h\nu \longrightarrow C_2 + H$	5	5%	5%	
$C_2H_2 + e \longrightarrow C_2 + H_2$	10	10%	10%	
$C_2H_2 + e \longrightarrow C_2H + H$	10	20%	20%	
$C_3H_2 + h\nu \longrightarrow C_3 + H_2$	5			30%
$C_3 + h\nu \longrightarrow C_2 + C$	5			30%
$C_3H_4 + e \longrightarrow C_3 + H_2$	10			50%
Remaining reaction rates	-	5%	5%	5%
Fit on profile	-	5%	5%	5%
Error on spatial profiles	-	10%	10%	10%

Table 19.6: Summary of the upper limits for the quantitative errors