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The effect of uncertainties on chemical models of dark clouds

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Abstract. The gas-phase chemistry of dark clouds has been studied with a treatment of uncertainties caused both by errors in individual rate coefficients and uncertainties in physical conditions. Moreover, a sensitivity analysis has been employed to attempt to determine which reactions are most important in the chemistry of individual species. The degree of overlap between calculated errors in abundances and estimated observational errors has been used as an initial criterion for the goodness of the model and the determination of a best 'chemical' age of the source. For the well-studied sources L134N and TMC-1CP, best agreement is achieved at so-called "early times" of $\approx 10^5$ yr , in agreement with previous calculations but here put on a firmer statistical foundation. A more detailed criterion for agreement, which takes into account the degree of disagreement, is also proposed. Poorly understood but critical classes of reactions are delineated, especially reactions between ions and polar neutrals. Such reactions will have to be understood better before the chemistry can be made more secure. Nevertheless, the level of agreement is low enough to indicate that a static picture of physical conditions without consideration of interactions with grain surfaces is inappropriate for a complete understanding of the chemistry.

Key words. Astrochemistry – ISM: abundances – ISM: clouds – ISM: molecules

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1. Introduction

The chemistry of dark clouds, now known as quiescent cores, has been studied for over thirty years (Herbst & Klemperer 1973; Watson 1973). Indeed, a significant fraction of the more than 130 gas-phase species detected via high-resolution spectroscopy in the interstellar and circumstellar media has been seen in such sources, which include the well-studied clouds TMC1-CP and L134N (Smith et al. 2004; Terzieva & Herbst 1998). In an attempt to reproduce the abundances of these species, a large number of gas-phase chemical models have been developed that compute the variation of the gas-phase concentrations as a function of time. For many years, most of these models were based on the pseudo-time-dependent approximation (Prasad & Huntress 1980; Leung et al. 1984; Langer et al. 1984; Millar & Nejad 1985), in which the chemistry evolves under fixed and homogeneous conditions from some initial abundances, consisting of totally atomic material except for a high abundance of H_2. In the last decade, more complex models, including surface chemistry (Hasegawa et al. 1992; Ruffle & Herbst 2000), heterogeneity of the source (Hartquist et al. 2001), and assorted effects of dynamics and turbulence (Markwick et al. 2000), have been reported.

In all of these models, the connections among gas-phase species are described by up to thousands of chemical reactions, with rates quantified by rate coefficients, most of which are poorly determined by experimental or theoretical means. Nevertheless, even the older pseudo-time-dependent models were at least partially successful in reproducing the exotic nature of the chemistry (molecular ions, radicals, and metastable isomers), the unsaturated nature of the more complex products (e.g., cyanopolyynes), and the strong deuterium fractionation. They have been less successful, however, in detailed comparisons with observations of fractional abundances and column densities for the large number of species observed in individual sources. In the last published comparison between a pseudo-time-dependent theory and observation for the well-studied source TMC1-CP (Smith et al. 2004), it was found that at the time of best agreement (1×10^5 yr), only about 2/3 of the observed species have calculated fractional abundances within an order-of-magnitude of the observed values. This result, obtained with the relatively new osu.2003 network and so-called "low-metal" elemental abundances, is actually worse than obtained with a previous network from the Ohio group, known as the "new standard model" (nsm), where nearly 4/5 of the molecular

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abundances were reproduced to within one order of magnitude (Terzieva & Herbst 1998). The order-of-magnitude criterion used in both studies is a subjective one, however, and no comparison involving TMC1-CP has ever been done by taking into account the rate coefficient uncertainties in the computation of the theoretical abundances.

Without any quantification of the random model error, it is difficult to conclude if observed abundances can be reproduced or not by the model. Indeed, including the estimated uncertainties in rate coefficients is the only way to define those species with abundances not reproduced by chemical networks. With a rigorous quantitative approach to uncertainty, moreover, one can begin to comprehend the deficiencies of gas-phase pseudo-time-dependent calculations, and determine where improvement is most necessary. If, for example, hydrogen-rich species, which may be synthesized on grain surfaces and desorbed into the gas via non-thermal means, are the only species with abundances to be poorly reproduced, the most important correction would involve the inclusion of surface processes. If, on the other hand, smaller species such as O_2 and H_2O, with simple chemistry, cannot be reproduced within the estimated errors, then it is at least conceivable that a far more complex physical scenario is needed in which the formation and dynamics of the quiescent core play roles in the chemistry (Bergin & Melnick 2005). Whether or not to give up on the pseudo-time-dependent approximation then depends critically on our estimates of uncertainties, because there is no point in violating Occam's Razor if a more simple theory is as adequate as a more complex one.

This paper is the second application of a method developed in Wakelam et al. (2005) to quantify the random errors of chemical models. In Wakelam et al. (2005), we presented the method in great detail and showed some consequences for hot core chemistry (T> 100 K). Hot cores occur during an evolutionary stage of star formation, and can have complex structures not well understood (Nomura & Millar 2004). Dark clouds, which have not yet started to collapse in an appreciable manner, may, on the contrary, have relatively simple temperature and density structures. These objects are then better laboratories to test the gas-phase chemical models usually used. In this paper, we apply the method to estimate the statistical errors as a function of time for dark cloud chemistry, which is occurring at an H_2 density of $\sim 10^4$ cm^{-3} and a temperature < 20 K. A previous analysis of uncertainties for mainly steady-state conditions was performed for dark clouds by Vasyunin et al. (2004), although their error was defined in a different manner.

The remainder of our paper is organized as follows. In Section 2, we briefly describe the chemical network and approach to uncertainties used for this study. Some general results are presented in Section 3, where we also (i) consider differences between the two major networks, and (ii) make a comparison between our uncertainty calculations and those of Vasyunin et al. (2004). Section 4 contains a comparison between our results and observed abundances towards the two dark clouds L134N and TMC1-CP, while Section 5 discusses the specific cases of O_2 and H_2O, and the cloud ages. We conclude the paper in Section 7.

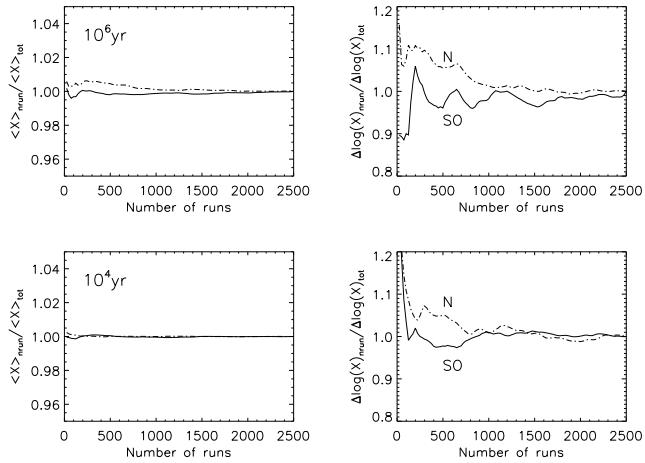

Fig. 1. Mean abundance ($< X >$) (left panels) and error $\Delta \log X$ (right panels) for N and SO plotted as a function of the number of runs. Both quantities are normalized by the value obtained for the maximum number of runs (2500). The results are given for Model 2 at two times: 10^4 yr on the lower panels and 10^6 yr on the upper panels.

Table 1. Physical parameters for the models.

Physical conditions	
Model 1	10 K, 10^4 cm^{-3a}
Model 2	5-15 K, $(0.5-1.5)\times 10^4$ cm^{-3a}
Model 3	5-15 K, $(0.5-1.5)\times 10^4$ cm^{-3a}, C/O=1.2

[a] H_2 density.

Table 2. Initial elemental abundances with respect to H_2.

Initial abundances			
He	2.8×10^{-1}	Fe^+	6.0×10^{-9}
N	4.28×10^{-5}	Na^+	4.0×10^{-9}
O	3.52×10^{-4}	Mg^+	1.4×10^{-8}
C^+	1.46×10^{-4}	P^+	6.0×10^{-9}
S^+	1.6×10^{-7}	Cl^+	8.0×10^{-9}
Si^+	1.6×10^{-8}		

2. Chemical network and uncertainty method

We used a time-independent physical model with the gas-phase chemical network osu.2003[1] reported by Smith et al. (2004). This network contains standard gas-phase reactions (ion-neutral, neutral-neutral, dissociative recombination etc), with the addition of a significant number of rapid radical-neutral processes. Except for H_2 production, the grains are only important as sites of negative charge that recombine with positive ions. We considered the un-

[1] http://www.physics.ohio-state.edu/~eric/research.html

certainties in all the classes of reactions except for ion recombination with negative grains. The uncertainties in the rate coefficients have recently been added to the osu.2003 network, based on those listed in the RATE99 network (Le Teuff et al. 2000)[2]. For the uncertainties not estimated at 10 K (according to the temperature range given in RATE99), we increased the uncertainty to a factor of 2.

The Monte Carlo method used here to include the rate-coefficient uncertainties is described in detail by Wakelam et al. (2005). Briefly, it consists of generating N new sets of rate coefficients by replacing each coefficient k_i by a random value consistent with its uncertainty factor F_i. We assume a normal distribution of $\log k_i$ with a standard deviation $\sigma_i = \log F_i$. We run the model for each set j, which produces, for each species, N values of the abundance $X_j(t)$ at a time t. The mean value of $\log X(t)$ gives us the "recommended" value while the dispersion of $\log X_j(t)$ around $< \log X(t) >$ determines the error due to kinetic data uncertainties. The error in the abundance $\Delta \log X = \frac{1}{2}(\log X_{\max} - \log X_{\min})$ is defined at a time t as the smallest interval $[\log X_{\min}, \log X_{\max}]$ that contains 95.4% of $\log X_j$ values, which is equivalent to 2σ for symmetric Gaussian distributions. For example, if $\Delta \log X = 1.0$ and the calculated distribution is symmetric, then the 2σ values of $X_{\max}$ and $X_{\min}$ are one order of magnitude greater and less than X, respectively. Similarly, if $\Delta \log X = 0.5$, the 2σ values are greater and less than X by a factor of 3.3, and if $\Delta \log X = 0.3$, they are greater and less than X by a factor of 2.0.

We initially ran two models with different physical conditions. In the first model (Model 1), the temperature and the H_2 density are held constant at values of 10 K and 10^4 cm^{-3}, respectively; only the rate coefficients vary. For the second model (Model 2), we randomly chose the temperature and the density within a possible range of values. This uncertainty was adopted for two reasons: (i) the cloud temperature and density are usually derived from observations (using approximate line excitation models) and an error in these values can usually be determined, and (ii) the modeled clouds are more likely to be inhomogeneous sources with contributions over the chosen ranges of temperature and density. We investigated the sensitivity of the results if an uncertainty of ±50% is considered for T and n(H_2) around the typical values given for Model 1 (see Table 1). Because temperature and density are physical parameters not characterized by a Gaussian distribution, we used a flat distribution instead for the rate coefficients. For both models, we used a cosmic-ray ionization rate of 1.3×10^{-17} s^{-1}, a visual extinction of 10 and the low-metal elemental abundances, which are listed in Table 2. A third model, with carbon-rich elemental abundances, is discussed later in the text.

For Model 1 and Model 2, we performed 2000 and 2500 different runs, respectively. In order to demonstrate convergence, we plot as examples in Fig. 1 the mean abundance $< X >$ and its error $\Delta \log(X)$ for the species N and SO as functions of the number of runs at two different times with Model 2. The plotted parameters are normalized by the values obtained for 2500 runs. For all the species, we noticed that the number of runs chosen is more than adequate.

[2] http://www.udfa.net

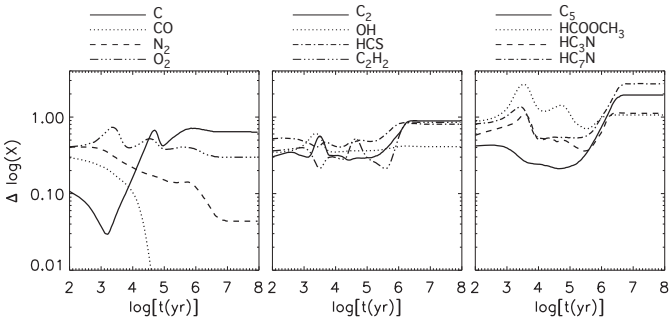

Fig. 2. Error $\Delta \log X$ as a function of time for some species with Model 1.

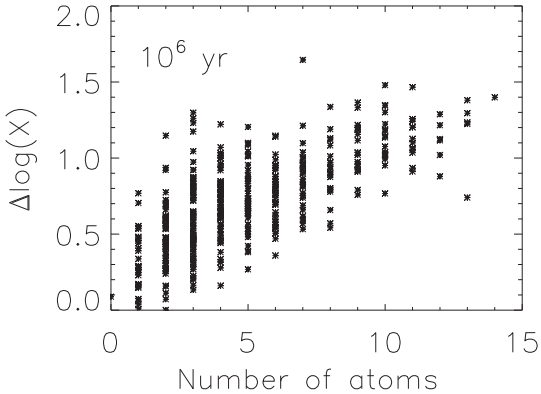

Fig. 3. Error, $\Delta \log X$, as a function of the number of atoms per molecule at 10^6 yr for Model 1.

3. Calculated uncertainties in abundances

3.1. General considerations

Figure 2 presents the error $\Delta \log X$ for some species as a function of time and for the physical conditions of Model 1 (see Table 1). As already noticed for hot core chemistry, the errors in the abundances increase with time for most of the molecules except the species that contain a dominant portion of an element, such as CO for carbon and N_2 for nitrogen. For example, the errors for HCN and HC_3N are 0.2 and 0.5 at 10^5 yr and increase to 0.3 and 1.1, respectively, at 10^7 yr. The error also increases with the complexity of the molecule, an effect previously noted by Vasyunin et al. (2004). This effect is shown in Fig. 3 for the physical parameters of Model 1 at a time of 10^6 yr. For molecules with 10 atoms, the figure shows that an error of 1.0, corresponding to a factor of 10, is in the middle of the range, while for molecules with five atoms, the median error is ≈ 0.7, corresponding to a factor of five.

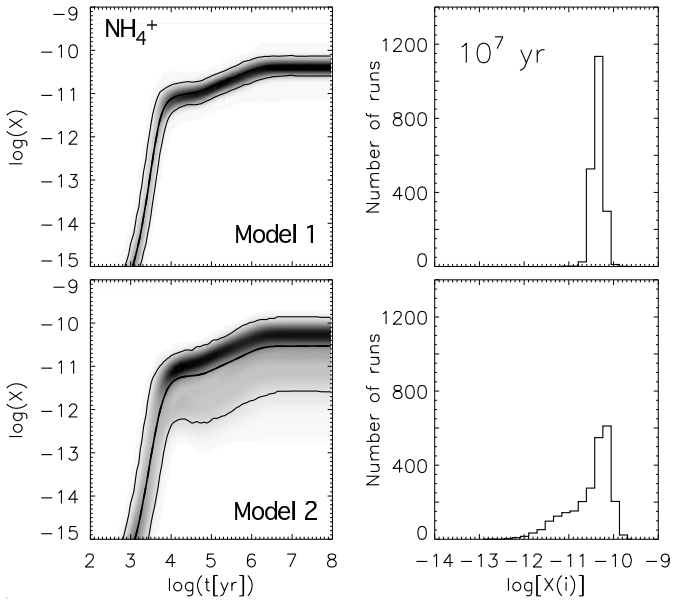

Fig. 4. Density of probability of the NH_4^+ abundance. The right plots represent the histograms of the abundance distributions at 10^7 yr. The top row is for Model 1 and the bottom for Model 2.

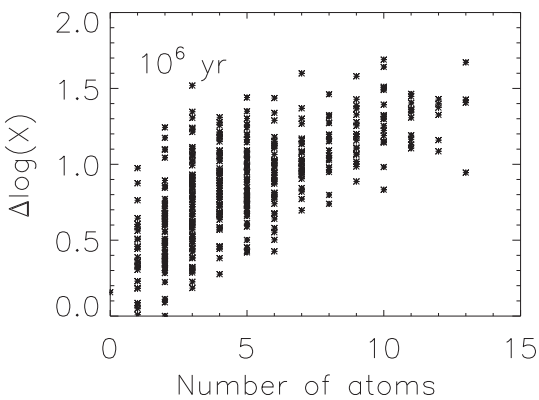

Fig. 5. Error, $\Delta \log X$, as a function of the number of atoms per molecule at 10^6 yr for Model 2.

3.2. Variation of the temperature and density

The variations of the gas temperature and density in Model 2 cause two major effects. First, they modify the distribution of the abundances at a given time from a Gaussian shape to an asymmetrical one, as can be seen by the example of NH_4^+ in Fig. 4. The effect is not surprising since the rate equations are not linear with respect to density or temperature. Indeed, the dependence on temperature can be exponential for processes with a small barrier. The second effect is an increase in the error, which can be significant for some of the species, as shown in Fig. 5, which is to be compared with Fig. 3. The nitrogen-bearing species are particularly sensitive to the variation of temperature and density, as can be seen by the examples in Table 3. What causes this extreme sensitivity? It is likely that the variation in temperature is the cause because the nitrogen chemistry starts with the reaction $N^+ + H_2 \rightarrow NH^+ + H$, which is assumed to be endothermic by 85 K in both the osu.2003 and RATE99 networks. The situation is more complex than can be contained in networks because it is likely that an estimated non-thermal fraction of H_2 in its J=1 *ortho* state of 10^{-3} drives the reaction and essentially converts all the atomic nitrogen ion into NH^+ (Le Bourlot 1991). Nevertheless, with the adopted rate coefficient, the reaction to form NH^+ is so inefficient at temperatures under 10 K that it loses importance. Thus, temperatures lower than 10 K lead to much lower abundances for some N-bearing species. The result is a skewing of the abundance distributions to lower values, as can be seen for the case of NH_4^+ in Fig. 4. The effect of the temperature and density variations is less important for complex molecules because the variations caused by the physical parameters are diluted by the large uncertainties due to the uncertainties in rate coefficients. For example, the uncertainties in the cyanopolyne abundances do not show a strong dependence on the physical parameters: the increase of $\Delta \log X$ with Model 2 is less than a factor of 2 for HCN and this number decreases with the increasing complexity of the cyanopolyne.

Table 3. Examples of errors computed using Model 1 ($\Delta \log X_1$) and Model 2 ($\Delta \log X_2$) at 10^5 yr.

Species	$\Delta \log X_1$	$\Delta \log X_2$
N^+	0.36	1.0
HNO	0.31	0.91
NH_3	0.27	0.88
NH_2CN	0.37	0.87
SO	0.64	0.79
H_2O	0.40	0.42
HC_3N	0.45	0.56
C_9N	0.43	0.53

3.3. Comparison between osu.2003 and RATE99 databases

The statistical uncertainties in the rate coefficients are not the only sources of error for gas-phase models. Most of the reactions have not been studied in the laboratory or via detailed theoretical considerations, so that approximate values for the rate coefficients must be used. Even studied reactions, if studied by more than one group, show large discrepancies in rates. Some of the problems in choosing proper rate coefficients can be seen in a comparison of the osu.2003 and RATE99 databases, which contain many reactions with different choices of rate coefficients. These differences arise from several specific sources:

a) Different estimates for poorly understood reactions such as radical-neutral reactions and both neutral-neutral and ion-molecule radiative associations,
b) Different choices of experimental values from uncritical compilations such as the NIST Chemical Kinetics

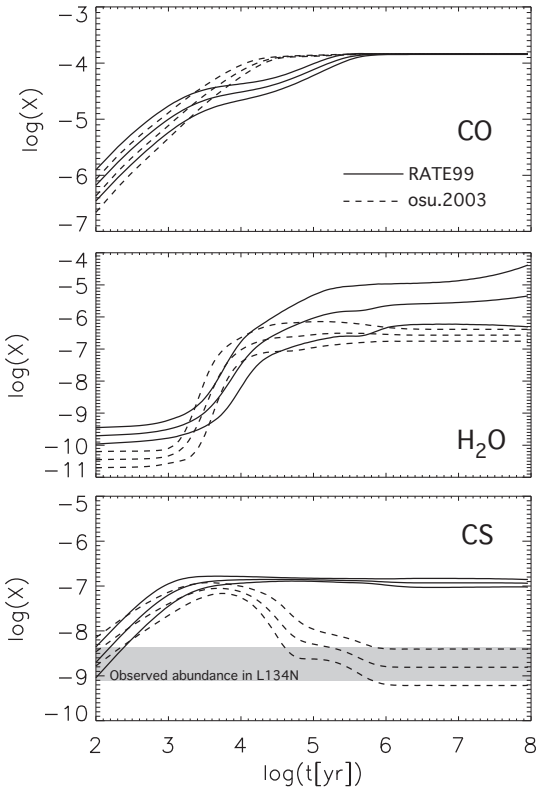

Fig. 6. CO, H_2O and CS abundances as a function of time computed using the osu.2003 (dashed lines) and the RATE99 (solid lines) databases. The three curves for each molecule and database refer to the average value and the 2σ errors.

Database (http://kinetics.nist.gov/index.php) or from competing measurements,

c) Different approximations regarding the temperature dependence of ion-polar neutral reactions.

The problem with radical-neutral reactions has been studied by Smith et al. (2004): the osu.2003 network includes estimates of rapid rates for a variety of such reactions that are greater than used in RATE99 as well as the previous network from the Ohio group. The last discrepancy derives from the fact that although experiments show that virtually all of the small number of ion-polar neutral reactions studied possess an inverse temperature dependence (Rowe 1992; Rowe & Rebrion 1992) this dependence is not easily expressible in terms of the simple rate expression used in the networks. Based on the work of Herbst & Leung (1986), the osu.2003 network uses an approximation derived from the locked dipole approximation for linear neutrals and classical scaling approach for non-linear neutrals (Su & Chesnavich 1982). Both of these approximations lead to a temperature dependence of $T^{-1/2}$, while the RATE99 network assumes the rate coefficients to have no temperature dependence. More detailed studies show that the inverse dependence of the rate coefficient on temperature may well be in between these two limiting cases (Neufeld et al. 2005). More work is clearly needed on these systems.

At 10 K, 60% of the reactions present in both databases show a difference in rate coefficient lower than the considered uncertainty, a condition which can be expressed as

$$\frac{k_{i1}/k_{i2}}{\sqrt{2}F_i} \leq 1, \quad (1)$$

where k_1 and k_2 are the rate coefficients from the different networks with $k_1 > k_2$ and F is the uncertainty factor. In other words, almost half of the common reactions show a difference in rate coefficient not covered by the uncertainties in the rate coefficients, with 2% of them having an "extra" difference greater than three orders of magnitude ($\frac{k_{i1}/k_{i2}}{\sqrt{2}F_i} > 1000$). These differences may not have strong consequences on the modeling results, however, if the reactions concerned are not important or if formation and depletion reactions in one model are both larger to a similar extent than in the other. So, one must ask whether or not the differences between the abundances computed with the two databases are larger than the errors due to rate coefficient uncertainties.

To answer this question, we ran Model 1 with the RATE99 network so as to compare with the osu.2003 results. We obtained distributions of results for abundances that do not always overlap at the 2σ level. In fact, eighty-four percent of the 373 common species show a disagreement at some times between the abundances computed with the two databases. No neutral species and only 62 ions, such as S^+, C_2^+, CN^+ and C_6^+, overlap at all times. Note that the differences are due to difference in the values of the rate coefficients and not in the differing reaction lists for the two networks, since we repeated the comparison with a list of reactions common in both databases and obtained similar results. Fig. 6 shows three examples: the CO, H_2O and CS molecules. The error in the abundance of CO at later times is very low because this molecule is the main reservoir of atomic carbon in the gas phase and both sets of reactions give the same results. At early times, between 6×10^3 and 2×10^5 yr, the abundance computed with osu.2003 is higher than the one computed with RATE99, reaching a ratio of 4 at 3×10^4 yr. The envelopes defined by the error in the rate coefficients do not overlap. For H_2O, the early and late abundances diverge by one order of magnitude and the envelopes do not quite overlap, whereas CS is produced to a much greater extent for the RATE99 case: the difference of up to 2 orders of magnitude at steady state far exceeds the envelopes of error. Indeed, with RATE99, CS is found to be the reservoir of S: the difference between the 2 networks is thus quite profound and not only quantitative.

We attempted to identify the reason for the discrepancy involving CS using the sensitivity method described in Wakelam et al. (2005). At 10^5 yr, of the 20 most important reactions in the calculation of CS with the osu database, 10 are different in RATE99 and for those 10, 7 are ion- polar neutral reactions. If we replace these 10

rate coefficients by their values in RATE99, the CS result approaches the RATE99 abundance to within a factor of ≈ 3. Thus, one would argue that the sensitivity approach works well in deducing both the "important" reactions in the osu calculation and the reason for the difference with the results from the RATE99 calculations. But, one must be cautious because different results are obtained if one starts with RATE99: here, because of their smaller rate coefficients, ion-polar neutral reactions play a less significant role in the production and destruction of CS. Indeed, the reactions of importance for CS are quite different in the two networks. The introduction of the osu rates for a small number of "important" reactions in the RATE99 network produces only a small change although the difference in the rate coefficients of these reactions is not covered by the uncertainty factor. The RATE99 abundance of CS is thus more stable against rate coefficient modifications, which shows that a large number of reactions would have to be modified in order to change the result.

For CO, which shows a factor of 3 difference at early times, we were not able to identify any main reactions responsible for this discrepancy. Once again, these small differences are then due to a large number of reactions with small variations of rate coefficients between the two databases.

3.4. Comparison of uncertainty calculations

Vasyunin et al. (2004) did a similar study on dark cloud chemistry to ours using a previous version of the RATE99 database with a flat distribution for the rate errors (see Wakelam et al. 2005, for a discussion concerning this point) and focused their results on the steady-state abundances. Although they defined the error in the abundance in a different way, we can compare their results with ours at 10^8 yr. The authors used the full width at half maximum (FWHM) of the histograms of $\log X$, which is $\sim \frac{2.35}{2}\Delta \log X$, as defined in Sect. 2, since most of the histograms have a Gaussian shape (see the discussion about the definition of the error in Wakelam et al. 2005). For most of the species, we found a lower uncertainty than did Vasyunin et al. (2004). As an example, the C_4 molecule has a $\Delta \log X$ of 1.45 at 10^8 yr in our study whereas Vasyunin et al. found an FWHM of 2-3 for carbon clusters. The reason for this difference appears to be mainly due to the database used, because we found that the errors are generally higher with RATE99 than with osu.2003, as can be seen in Fig. 6 for the case of H_2O. For the specific case of the molecule C_4, we calculate that $\Delta \log X$ is 2 at 10^8 yr with RATE99, a value well above what we calculate with osu.2003. The source of this difference in errors is unclear.

4. Comparison with observations

We have compared our theoretical results with some observations in two dark clouds: L134N (N position) and TMC-1 (CP peak). The abundances observed in L134N are summarized in Table 4 while those observed in TMC-1CP are listed in Smith et al. (2004, Table 3). The goal of this comparison is to take into account both the uncertainty in the observed values and in the chemical modeling. For the observed abundances, since all the abundances are not given with their corresponding errors, we assumed a standard uncertainty of $\pm$ a factor of 3 for the following reasons. First, telescope and atmospheric calibrations are responsible for $\sim 30\%$ of uncertainty in the observed abundances. In addition, the abundances relative to H_2 depend on the H_2 column density, which is an additional

Table 4. Observed abundances towards L134N.

Species	$N(i)/N(H_2)$	Ref	Species	$N(i)/N(H_2)$	Ref
CH	1(-8)	(1)	CN	8.2(-10)	(1)
CO	8.(-5)	(1)	CS	1.7(-9)	(2)
NO	6.(-8)	(1)	OH	7.5(-8)	(1)
SO	3.1(-9)	(2)	C_2H	$\leq 5.(-8)$	(1)
C_2S	6.(-10)	(1)	H_2S	8.(-10)	(1)
HCN	1.2(-8)	(2)	HNC	4.7(-8)	(2)
OCS	2.(-9)	(1)	SO_2	$\leq 1.6(-9)$	(2)
C_3H	3.(-10)	(1)	C_3N	$\leq 2.(-10)$	(1)
C_3O	$\leq 5.(-11)$	(1)	C_3S	$\leq 2.(-10)$	(1)
H_2CO	2.(-8)	(1)	H_2CS	6.(-10)	(1)
NH_3	9.1(-8)	(1)	CH_2CN	$\leq 1.(-9)$	(1)
C_2H_2O	$\leq 7.(-10)$	(1)	C_3H_2	2.(-9)	(1)
C_4H	1.(-9)	(1)	HCOOH	3.e-10	(1)
HC_3N	8.7(-10)	(2)	CH_3CN	$\leq 1.(-9)$	(1)
CH_3OH	3.7(-9)	(2)	CH_3CHO	6.(-10)	(1)
C_2H_3CN	$\leq 1.(-10)$	(1)	C_3H_4	$\leq 1.2(-9)$	(1)
HC_5N	1.(-10)	(1)	HC_7N	2.(-11)	(1)
HCO^+	1.(-8)	(2)	HCS^+	6.(-11)	(1)
N_2H^+	6.8(-10)	(2)	H_2CN^+	$\leq 3.1(-9)$	(1)
H_2O	$\leq 3.(-7)$	(3)	O_2	$\leq 1.7(-7)$	(4)
C^0	$\geq 1.(-6)$	(5)			

[a] $a(-b)$ refers to $a \times 10^{-b}$
(1) Ohishi et al. (1992)
(2) Dickens et al. (2000)
(3) Snell et al. (2000)
(4) Pagani et al. (2003)
(5) Stark et al. (1996)

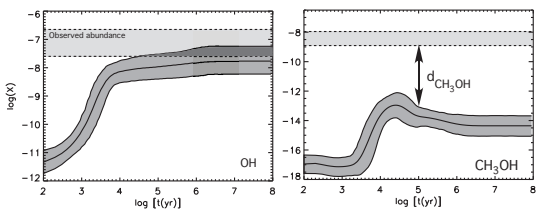

Fig. 7. Theoretical abundance of OH (left) and CH_3OH (right) as a function of time for Model 2. The dashed lines represent the observed values in L134N with an error of a factor of 3. The agreement between the observed and modeled abundance of OH is shown as a dark area whereas the disagreement for CH_3OH is quantified by a distance of disagreement d (see Sect. 5.2).

Table 5. Fraction of species reproduced by the different models and databases with the mean time of best agreement (expressed logarithmically).

		Factor 3		
		Model 1	Model 2	Model 3
L134N	osu.2003	73%, 5.7	80%, 4.8	78%, 4.7
	RATE99	78%, 5.8	83%, 5.9	66%, 4.7
TMC-1	osu.2003	57%, 4.4	61%, 4.4	76%, 4.9
	RATE99	68%, 5.2	70%, 5.7	70%, 5.5
		Factor 5		
		Model 1	Model 2	Model 3
L134N	osu.2003	82%, 4.6	87%, 4.7	85%, 4.8
	RATE99	83%, 4.8	83%, 6.0	74%, 5.2
TMC-1	osu.2003	61%, 4.4	67%, 4.4	86%, 4.9
	RATE99	72%, 5.6	78%, 5.6	76%, 5.3

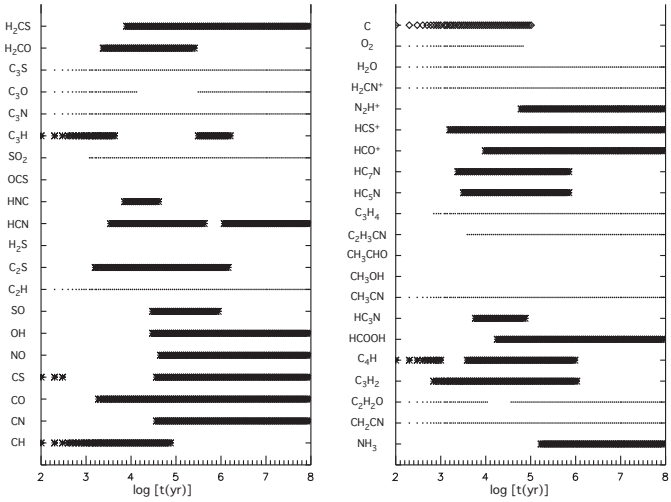

Fig. 8. Agreement between the observed abundances towards L134N "N" peak) and the predictions of the chemical model (Model 2) as a function of time. Symbols indicate an agreement between the observational constraint and the model results. Stars are for the observed abundances whereas dots and diamonds are for the observational upper and lower limits respectively.

source of uncertainty. The H_2 column density is usually indirectly determined from the emission of other molecules via LTE, LVG, or Monte-Carlo models and usually different molecules give different estimates of H_2 densities. Indeed, the emission of the molecules may come from different the layers of gas. In TMC-1CP for instance, it appears that $C^{18}O$ may not come from the same volume of gas as the other molecules and the abundances compared to H_2 may be overestimated (Pratap et al. 1997). Another reason for the high uncertainty of the observed values is that the inventory of the observed abundances come from several studies, in which several telescopes and approximations were used to compute the observed abundances, resulting in disagreements by at least a factor of three for some species. As a specific example, the SO abundance towards L134N (N position) is 3.1×10^{-9} in Dickens et al. (2000) whereas it is 6 times higher in Ohishi et al. (1992). Even though we think that an uncertainty of $\pm$ a factor of 3 is reasonable, and consider it to be our standard observational uncertainty, we also use a larger uncertainty of $\pm$ a factor of 5 to consider its effect.

For the chemical model, we considered both the uncertainties in the rate coefficients and in the physical conditions, using Model 2 for both clouds. To compare the observed and modeled values, we first define agreement between the model and the observations to occur when the error bars of the calculated and observed values overlap. A more detailed approach is discussed below in Section 5.2. An example of overlapping error bars at certain times only can be seen in Fig. 7 for the case of OH in L134N, where the overlap is shown as a darker region.

4.1. Results for L134N

Figure 8 shows the times of agreement for each observed molecule towards L134N. With our standard uncertainty of a factor of three in the observed abundances, Model 2 reproduces up to roughly 80% of the 41 observed molecules in the range of times $(6.0 - 6.8) \times 10^4$ yr and the level of agreement tapers off gradually at both younger and older ages. The peak number increases to 87% if an error of a factor of 5 is taken for the observed values. Model 1 reproduces fewer species (73%), and the best agreement occurs later, at 5×10^5 yr (see Table 5). With Model 2, the molecules H_2S, OCS, CH_3OH, CH_3CHO are underestimated at all times. On the other hand, the observed abundances of HNC, C_3H, C_3O and NH_3 are reproduced by the model but not at the best range of ages. The three species C_3H, HNC, and NH_3 are in agreement with observation for times very close to the best range, while C_3O has not been detected and only an upper limit is known. The special cases of O_2 and H_2O, for which upper limits have been well studied, are discussed in Sect. 5.1.

4.2. Results for TMC-1

Using Model 2, we can only reproduce at best 50% of the observed 52 molecular abundances in the CP peak of TMC-1. This percentage is even lower than the 67% obtained by Smith et al. (2004), who compared the results of the osu.2003 database with the same observations towards TMC-1CP. These authors considered the modeling to be successful if the differences between the observed and theoretical values are less than a factor of 10. Smith et al. (2004), Terzieva & Herbst (1998) and Roberts & Herbst (2002) showed that by increasing the C/O elemental ratio, they were able to better reproduce the observations. We then ran a third model (Model 3, see Table 1) identical with Model 2 except that the initial abundance of O is lowered to 1.2×10^{-4}, so that the elemental C/O ratio becomes 1.2. Fig. 9 shows the comparison with Model 3. Here, seventy-six percent of the molecules are reproduced

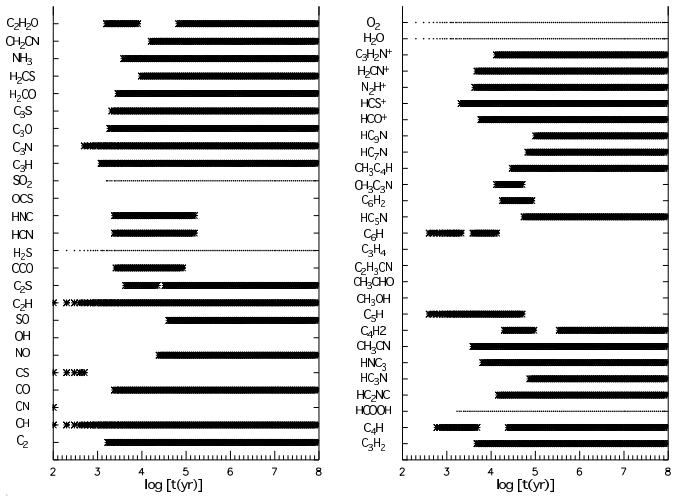

Fig. 9. Agreement between the observed abundances towards TMC-1 ("CP" peak) and the predictions of the chemical model (Model 3) as a function of time.

considering an observed uncertainty of a factor of 3 at a time of 8×10^4 yr. This number is increased to 86% at the same age for an observed uncertainty of a factor of 5. The molecules OH, OCS, CH_3OH, CH_3CHO, C_2H_3CN and C_3H_4 are never reproduced by the model whereas the CN, CS, C_5H, HC_9N, C_6H and CH_3C_3N abundances are not reproduced in the optimum age range. The observed abundance of OH in TMC-1 is quite uncertain since it was detected using a significantly larger beam than for the other species, and contamination from other regions of the cloud is probable (Ohishi et al. 1992).

Looking at both clouds, we see that the abundance of the molecules OCS, CH_3OH and CH_3CHO are underestimated at all times by the model compared with the observed values. One explanation could be these species are formed on the grains and released in the gas phase by non-thermal processes (Markwick et al. 2000). Indeed, OCS and CH_3OH are known to be present on the grain mantles with an abundance (comparable to that of H_2) of $\sim 10^{-7}$ for OCS (Palumbo et al. 1997) and $\sim 10^{-6}$ for CH_3OH (Chiar et al. 1996). Work in progress by Garrod et al. (submitted) with a gas-grain model and various non-thermal desorption mechanisms supports this view. The fact that H_2S and NH_3 are not reproduced correctly in L134N may have the same origin since H-enriched molecules are believed to form efficiently on grains although solid H_2S has never been detected on grains (van Dishoeck & Blake 1998). For H-poor species such as CS, CN and HNC, some of the rate coefficients of the critical reactions forming and depleting them may be more uncertain than we have assumed, especially if the reactions have not been studied and the estimated uncertainties are hiding non-random errors.

For the case of the two cold cores studied using osu.2003, as opposed to our previous study of hot cores, we find that with our sensitivity technique it is most often difficult to isolate small numbers of very important reactions for those molecules with abundances we cannot reproduce. Rather, the general picture is that for many species, there are large numbers of reactions that are of relatively equal importance.

There are some reactions deemed important by our sensitivity technique that are critical for all the species: these are the ionization of H_2 and He by cosmic rays, as already noticed by Vasyunin et al. (2004)and Wakelam et al. (2005), and raised in an oral presentation by A. Markwick-Kemper in the 16th UCL Astronomy Colloquium (Windsor, UK, 2002). Ionization reactions involving cosmic rays, both direct and indirect, are, however, better thought of as variable parameters rather than reactions with uncertain rates since it not in general the physics of the process but the flux of cosmic rays that is in doubt.

4.3. RATE99 calculations

Before definitively ascribing the disagreements to specific causes, it is useful to see how the comparison with observations is affected by the use of the RATE99 network. Table 5 lists the overall level of agreement for both networks. On balance, the results with RATE99 show slightly better agreement with observation and show it at later times. Unlike the osu.2003 results, the RATE99 results are in agreement for the saturated species methanol and, in some cases, acetaldehyde. Although this agreement would appear to weaken our argument that the saturated species are produced on grain surfaces, it should be noted that the methanol prediction of RATE99 is almost certainly wrong because the gas-phase synthesis of methanol used:

$$CH_3^+ + H_2O \longrightarrow CH_3OH_2^+ + h\nu, \quad (2)$$

$$CH_3OH_2^+ + e^- \longrightarrow CH_3OH + H, \quad (3)$$

is assumed to be far too efficient for at least three reasons: (i) the radiative association reaction to produce the precursor ion $CH_3OH_2^+$ has been measured to occur much more slowly than predicted (Lucas et al. 2002), (ii) the dissociative recombination of this ion leads to methanol in only 6% of collisions (Geppert et al. 2006), and (iii) the water abundance used in the radiative association reaction is far greater than its measured upper limit. New calculations using the RATE99 network now agree with the osu.2003 result that this species cannot be produced in the gas (Geppert et al. 2006).

The case of acetaldehyde may or may not be similar. This species is also thought to be produced via a radiative association

$$H_3O^+ + C_2H_2 \longrightarrow CH_3CHOH^+ + h\nu, \quad (4)$$

followed by a dissociative recombination (Herbst 1987):

$$CH_3CHOH^+ + e^- \longrightarrow CH_3CHO + H. \quad (5)$$

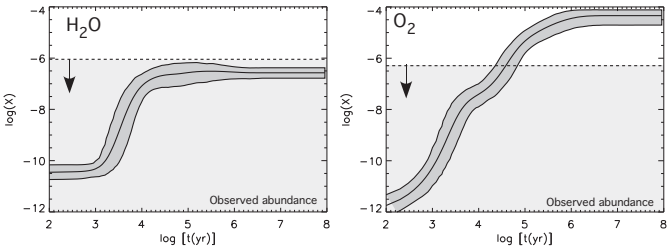

Fig. 10. Comparison between the theoretical abundances with error bars of H_2O and O_2 (Model 2) and the upper limits of the abundances found in L134N (see Table 4)

There is no direct evidence for either reaction, although the association does occur at high densities in the laboratory via collisional stabilization (Herbst 1987).

We conclude that there is substantial evidence that methanol is only produced on grains, although the case against gas-phase production of acetaldehyde is not quite proven. It is likely though that the high abundance of acetaldehyde in the RATE99 calculation stems at least partially from an overly slow destruction by ions since this species has a dipole moment. The percentages of species in agreement using the RATE99 database listed in Table 5 do not include the agreement with these two species.

5. Discussion

5.1. Special cases of water and molecular oxygen

An interesting result of this work is that it provides another manner in which the low upper limits to the abundances of gas-phase H_2O and O_2 in cold cores, detected by the SWAS and Odin satellites, can be explained (Snell et al. 2000; Pagani et al. 2003). Essentially, the upper limit of the observed abundance (multiplied by a factor of three given our standard chosen observational uncertainties) must not be less than the lower error bar of the theoretical abundance.

Let us first consider the case of L134N. In Fig. 10, we plot the calculated Model 2 abundances for water and oxygen with error bars as functions of time and superimpose the measured upper limits multiplied by a factor of three. The results show that both species are successfully reproduced in the optimum age range defined by the maximum agreement with all species, although the case of O_2 is much more marginal since it is clearly overproduced at times after 10^5 yr. This result shows that interaction with grain surfaces is not necessarily required if we consider young clouds ($\leq 10^5$ yr). The abundance of O_2 was found, however, to be lower than the value for L134N ($< 10^{-7}$) in a dozen dark clouds (Pagani et al. 2003), which we expect to have different ages. It may then be necessary to invoke depletion processes to explain the low abundance of O_2 in quiescent cores (see Roberts & Herbst 2002). The case of TMC-1 is singular since we used a model (Model 3) with high elemental C/O ratio. Here there are no age constraints (see results in Fig. 9).

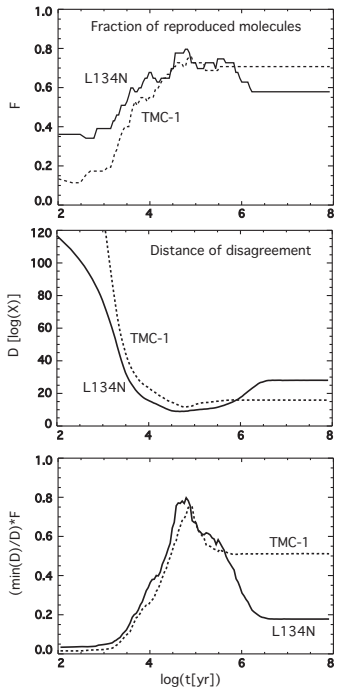

Fig. 11. Upper panel: the fraction of molecules reproduced by the model as a function of time for both clouds (Model 2 for L134N and Model 3 for TMC-1). Middle panel: the distance D of disagreement between the observed and modeled abundances (see text for details). Lower panel: the fraction of reproduced molecules multiplied by min(D)/D (minimum of the distance of disagreement divided by the distance of disagreement). We consider a factor of 3 uncertainty in the observed abundances.

5.2. Age of the clouds: a more refined estimate

Our models of quiescent cores are clearly not the complete picture since dynamical forces are producing and destroying cores while chemistry occurs (Garrod et al. 2005). For TMC-1 and L134N, the creation and chemistry have been occurring to some extent simultaneously. So, our pseudo-time-dependent calculations represent a crude approximation, with frankly an uncertain zero-time condition. Even within this crude approximation, we have used a less than perfect criterion to determine the "chemical" age for TMC-1CP and L134N by simply maximizing the number of molecules with calculated abundances and error bars in agreement with observed values. Essentially, we have made no allowance for the quality of the agreement and the extent of the disagreement for individual species. The results of this simple method are re-plotted in the top panel of Fig. 11 for L134N (Model 2) and TMC-1CP (Model 3) as the fraction F of molecules in agreement vs time. In this representation, we can see that the best age for L134N is somewhat more distinct that for TMC-1CP, but that the optimum ages lie in what previously was known as "early time", well before steady-state conditions set in.

To do somewhat better, we first compute an arbitrary parameter called the distance of disagreement D, which is defined, for the species not reproduced by the model, as the sum over all species of the distance d_i (in units of $\log X$, see Fig. 7) between the observational value and the theoretical one. For example, if for a particular species, i, $X_{obs} > X_{model}$ then the contribution to D is given by the expression

$$d_i = \log X_{\mathrm{obs;min}} - \log X_{\mathrm{model;max}}, \quad (6)$$

where the maximum and minimum values refer to the error bars. The middle panel of Fig. 11 shows the total distance D as a function of time for the two clouds. This plot indicates that the disagreement with the model reaches a minimum, labeled min(D), somewhat after 10^4 yr. Finally, the lower panel of Fig. 11 shows a plot vs time of the ratio between the minimum distance, min(D), and D, multiplied by the fraction of reproduced molecules, F. This quantity, which includes the strength of individual disagreements for specific species, tends to sharpen the best age, especially for L134N. In particular, we obtain a sharp maximum for L134N around 6×10^4 yr and a less marked maximum for TMC-1CP around 10^5 yr. These numbers are not strikingly different from a variety of other estimates, but must be taken with extreme caution. The ages derived analogously with the RATE99 set of reactions are somewhat larger, $\sim 10^6$ yr.

6. Conclusions

In this paper, we have reported the use of our Monte Carlo approach to uncertainties in calculated abundances to study the gas-phase chemistry of dark clouds, in particular the well-studied sources TMC-1CP and L134N. We have utilized models in which the uncertainties in both rate coefficients and physical conditions are included; the latter can be thought of as either the actual observational uncertainties or physical heterogeneities in the sources. With a specific criterion for agreement between observation and theory in which the errors in both techniques must overlap, we find that most but not species detected in the sources are reasonably well accounted for at so-called "early time," a far from novel result although one determined more rigorously than in previous approaches.

A major goal of the study has been to gain some insight as to which failing of the simple picture utilized is the more important: the lack of grain-surface chemistry or the lack of a dynamical model of the sources. For saturated (H-rich) species, with reasonably understood syntheses on grain surfaces, our results support earlier indications that surface chemistry is an important, probably a critical omission, but for unsaturated species, the picture remains less clear because it is difficult to determine from our sensitivity analysis whether the discrepancies can be accounted for by poorly determined rates of critical chemical reactions. This difficulty stems from the fact that the chemistry of unsaturated species often seems to involve contributions from large numbers of poorly determined reaction rates.

The fact that discrepancies for the calculated abundances of individual species between two chemical networks used, our osu.2003 network and the RATE99 network, can be larger than their calculated random uncertainties indicates that more attention must be paid in the laboratory to specific classes of reactions, such as ion-polar neutral systems, before more definitive conclusions can be reached. Further complicating the issue are other concerns such as the proper initial make-up of the gas, what elemental abundances are reasonable, and the range over which the cosmic ray ionization rate ζ can be varied. Nevertheless, our study indicates strongly that gas-phase models of static sources cannot represent the complete picture. More complex treatments, involving cycles of surface adsorption, reaction, and desorption, possibly coupled with dynamical histories of the sources, would appear to be required.

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