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New quantum chemical computations of formamide deuteration support gas-phase formation of this prebiotic molecule

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ABSTRACT

Based on recent work, formamide might be a potentially very important molecule in the emergence of terrestrial life. Although detected in the interstellar medium for decades, its formation route is still debated, whether in the gas phase or on the dust grain surfaces. Molecular deuteration has proven to be, in other cases, an efficient way to identify how a molecule is synthesized. For formamide, new published observations towards the IRAS16293-2422 B hot corino show that its three deuterated forms have all the same deuteration ratio, 2–5 per cent and that this is a factor of 3–8 smaller than that measured for H_2CO towards the IRAS16293-2422 protostar. Following a previous work on the gas-phase formamide formation via the reaction $NH_2 + H_2CO \rightarrow HCONH_2 + H$, we present here new calculations of the rate coefficients for the production of monodeuterated formamide through the same reaction, starting from monodeuterated NH_2 or H_2CO. Some misconceptions regarding our previous treatment of the reaction are also cleared up. The results of the new computations show that, at the 100 K temperature of the hot corino, the rate of deuteration of the three forms is the same, within 20 per cent. On the contrary, the reaction between non-deuterated species proceeds three times faster than that with deuterated ones. These results confirm that a gas-phase route for the formation of formamide is perfectly in agreement with the available observations.

Key words: ISM: abundances – ISM: molecules.

1 INTRODUCTION

Among the zoo of detected interstellar molecules, formamide ($HCONH_2$) has a peculiar role in prebiotic chemistry because it can generate both genetic and metabolic molecules (e.g. Saladino et al. 2012). It has been speculated that formamide could have been brought in large quantities on Earth from the interstellar/planetary dust and comets that rained on primitive Earth. Recent observations in star-forming regions (e.g. Lopez-Sepulcre et al. 2015) and, in particular, in regions that will eventually form stars like the Sun and planetary systems like the Solar system (e.g. Kahane et al. 2013; Mendoza et al. 2014) are in favour of this scenario. Kahane et al. (2013) have also found that the relative abundances of formamide and water, [$HCONH_2$]/[H_2O], in the solar-type protostar IRAS16293-2422 (hereinafter IRAS16293) and in the coma of the comet Hale-Bopp are very similar. Furthermore, Jaber et al. (2014) have found that formamide abundance shows an increase by more than two orders of magnitude in the interior of IRAS16293, in the so-called hot corino region. There, the formamide abundance is $\sim 6 \times 10^{-10}$, equivalent to a mass of more than 10 Mediterranean seas.

One peculiar aspect of the solar-type star-forming regions is the largely enhanced deuterium fractionation observed in H-bearing molecules (e.g. Ceccarelli et al. 2014). Indeed, the deuteration of molecules formed in the first cold prestellar phase can be several orders of magnitude larger than the statistical value based on the elemental D/H ratio (1.5×10^{-5}; Linsky 2007). Emblematic examples are those of formaldehyde and methanol, where the doubly (and even triply, for methanol) deuterated forms have been detected with D-bearing/H-bearing ratios up to 30 (and 5) per cent (e.g. Ceccarelli et al. 1998; Parise et al. 2003, 2006). Interestingly, the deuteration ratio in different molecules might provide the temporal sequence of their formation and, possibly, information on their synthetic route (e.g. Caselli & Ceccarelli 2012; Ceccarelli et al. 2014).

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Very recently, Coutens et al. (2016; hereinafter CJW2016) have reported the detection of deuterated formamide in the solar-type protostar IRAS16293 (see Jorgensen et al. 2016 and Jaber Al-Edhari et al. 2017 for a recent description of the source). In their work, CJW2016 detected the three forms of deuterated formamide: trans- and cis-HCONHD and $DCONH_2$. They found that they have approximately the same deuteration ratio, 2-5 per cent. Note that the latter observations have been obtained with the ALMA interferometer and that they refer to the hot corino region only. CJW2016 noticed that the fact that the three forms have a similar deuteration ratio provides constraints on the synthesis of formamide. Different routes have been suggested in the literature: the gas-phase reaction $NH_2 + H_2CO$ (Barone et al. 2015; Vazart et al. 2016), grain-surface radical recombination (e.g. Fedoseev et al. 2016) and synthesis dominated by UV or ion irradiation of ices containing various species, (e.g. Jones et al. 2011; Kanuchova et al. 2016). CJW2016 noted that the relatively small percentage of deuterated formamide with respect to formaldehyde might suggest a preference for synthesis on ice, as gas-phase routes should mostly retain the deuteration ratio of parent molecules.

However, this is not necessarily true. First of all, even though all the isotopologues are characterized by the same electronic energies, the reaction rate coefficients for the isotopic variants can be influenced by factors such as zero-point energies (ZPE) and densities of states. In addition, the reaction mechanism controls whether D or H displacement is favoured in gas-phase reactions involving partially deuterated species. In particular, the release of D over H can be favoured in direct abstraction processes, while the release of H over D is favoured in indirect reactions involving partially deuterated species. Also, the details of the reactive potential energy surface can change these common-sense rules (Skouteris et al. 1999).

In this Letter, we present new computations on the gas-phase reaction between partially deuterated amidogen (NH_2) and partially deuterated formaldehyde (H_2CO) and discuss the implications for the abovementioned astronomical observations.

2 GAS-PHASE FORMATION OF FORMAMIDE

The occurrence of the $NH_2 + H_2CO$ reaction as a source of formamide was first suggested by Kahane et al. (2013) but no measurements or computations were available at the time. Later, Barone et al. (2015) carried out accurate electronic structure calculations coupled with capture theory and RRKM kinetic calculations to estimate the rate coefficient. They found that the reaction can be very fast also in the cold interstellar conditions. This result was later confirmed by even more accurate computations by Vazart et al. (2016). According to these first studies, the reaction proceeds with the formation of a bound intermediate and, therefore, emission of H over D should be favoured. Interestingly, before the formation of the addition intermediate, a van der Waals complex is formed and a transition state has to be surmounted to form the addition intermediate (see Fig. 1). A second transition state connects the bound intermediate to the final products. It should be noted that, for this particular case, the vicinity of the energy levels of the transition states and the reactant asymptotes is a real computational challenge because the status of the transition states as 'emerged' or 'submerged' can fall within the uncertainty of the calculations (see Fig. 1). In Barone et al. (2015) and Vazart et al. (2016), the presence of the van der Waals complex has been deliberately neglected (see below). In a recently published theoretical paper on the formation of formamide on ice, a much smaller estimate of the rate coefficient was reported for the $NH_2 + H_2CO$ reaction (Song & Kastner 2016) because the energy level of the transition state connecting the van der Waals complex to the addition intermediate with the inclusion of its ZPE was found to be significantly above the reactant asymptote. In this paper, we clarify further the choice of neglecting the formation of the van der Waals complex. In addition, since the substitution of an H atom by a D one affects the density of states of all intermediates and transition states, as well as the tunnelling efficiency, a thorough investigation of the $NHD + H_2CO$ and $NH_2 + HDCO$ reactions is presented here to derive the specific rate coefficients and to assess whether they are compatible or not with formamide formation in the gas phase through the above reactions.

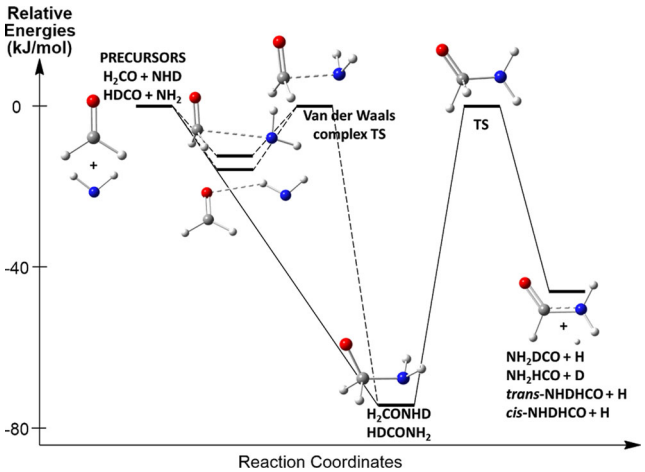

Figure 1. Complete reaction path for the $H_2CO + NHD \rightarrow NHDHCO + H$ and $HDCO + NH_2 \rightarrow NH_2DCO + H$ processes.

In particular, we consider the following isotopologues.

(1) NH_2+HDCO → $DCONH_2$+H, $\Delta H_0^\circ = -47.29$ kJ mol^{-1}
(2) NH_2+HDCO → $HCONH_2$+D, $\Delta H_0^\circ = -39.07$ kJ mol^{-1}
(3) NHD+H_2CO → t-HCONHD+H, $\Delta H_0^\circ = -48.49$ kJ mol^{-1}
(4) NHD+H_2CO → c-HCONHD+H, $\Delta H_0^\circ = -48.50$ kJ mol^{-1}

The exothermicities given above have been computed as described in Section 3. For each of the two monodeuterated versions of the reactants, there are two possible products to consider. In the case of HDCO, both normal and C-deuterated formamide are formed. In the case of NHD, HCONHD can be formed in the cis or trans isomers (hindered rotation around the C–N bond).

3 COMPUTATIONAL DETAILS AND RESULTS

The main body of the calculations has been performed with a development version of the Gaussian suite of programs (Frisch et al. 2015). The computations have been carried out using the double-hybrid B2PLYP functional (Grimme 2006), in conjunction with the m-aug-cc-pVTZ basis set (Dunning 1989; Papajak et al. 2009), where d functions on hydrogens have been removed. Semi-empirical dispersion contributions have also been included in DFT computations by means of the D3 model of Grimme, leading to the B2PLYP-D3 functional (Goerigk & Grimme et al. 2011; Grimme, Ehrlich & Goerigk 2011). Full geometry optimizations, and calculations of frequencies and rotational constants, have been performed for all minima and transition states of all isotopomers, also checking the nature of the obtained structures by diagonalizing their Hessians that have been used also to evaluate ZPEs at the harmonic level. Additional calculations based on coupled-cluster methods have been performed in order to reevaluate the energies of all species. The coupled-cluster singles and doubles approximation augmented by a perturbative treatment of triple excitations (CCSD(T); Raghavachari et al.

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Table 1. Summary of the energy of each species involved in the deuterated versions of the $NH_2 + H_2CO$ reaction. Each energy is given in hartree and in parentheses is given its relative energy with respect to the reactants in kJ mol^{-1}. The first column is the purely electronic (isotope independent) energy, while the others include zero-point contributions.

Species	Electronic energy	ZPE corrected (X=H,Y=D)	ZPE corrected (X=D,Y=H)
NHX + HYCO	− 170.367 866 (0.00)	− 170.324 839 (0.00)	− 170.324 535 (0.00)
HYCONHX	− 170.396 176 (−74.33)	− 170.344 028 (−50.38)	− 170.344 203 (−51.64)
Transition state	− 170.368 405 (−1.41)	− 170.323 737 (2.89) ($DCONH_2$)	− 170.323 873 (1.74) (cis)
		− 170.321 363 (9.13) ($HCONH_2$)	− 170.323 877 (1.73) (trans)
Products	− 170.385 371 (−45.96)	− 170.342 852 (−47.29) ($DCONH_2$)	− 170.343 008 (−48.50) (cis)
		− 170.339 721 (−39.07) ($HCONH_2$)	− 170.343 005 (−48.49) (trans)

1989) has been employed in conjunction with extrapolation to the complete basis set limit and inclusion of core-correlation effects (CCSD(T)/CBS+CV). At this level of calculations, the energy level of the van der Waals transition state is slightly above the energy of the reactants' asymptote (see Table 1). However, when a full treatment of triple (fT) and quadruple excitations (fQ) is also included, thus leading to the CCSD(T)/CBS+CV+fT and CCSD(T)/CBS+CV+fT+fQ approaches, the barrier issuing from this transition state significantly decreases (3.6 kJ mol^{-1} drops to 2.05 kJ mol^{-1} with full-T and to 1.67 kJ mol^{-1} with full-T and full-Q).

As in previous work (Barone et al. 2015), we have used the results of the electronic structure calculations to derive the capture theory rate constant for the formation of the initial bound intermediate (slightly dependent on the reduced mass). Subsequently, using the RRKM scheme as in previous work (Balucani et al. 2012, Leonori et al. 2013, Vazart et al. 2015a), we have calculated rate constants (as a function of energy) for the elimination of an H or a D atom leading to the formation of formamide. We have also calculated (using detailed balance) the energy-dependent rate constant for back-dissociation of the intermediate to the reactants as done in Vazart et al. (2015b) and Skouteris et al. (2015). The master equation has been solved as a function of energy to determine the bimolecular rate constant for formamide formation and its isotopologues. Finally, Boltzmann averaging has been carried out to determine rate constants as a function of temperature. Each rate constant has been fitted to the rate law:

$$k(T) = A \times (T/300K)^{\beta} \times e^{-\gamma/T} \quad (1)$$

The results are listed in Table 2 together with those of the undeuterated case (from Vazart et al. 2016) for comparison.

4 RESULTS AND DISCUSSION

The interaction between the reactants starts with the formation of a shallow van der Waals complex and the subsequent formation of a bound intermediate. This can then eliminate an H atom to form formamide or back-dissociate to the reactants. The electronic potential energy surface is the same for all isotopomers, but the energy levels, vibrational frequencies, rotational constants and zero-point energies depend on the masses involved. This can change the relative densities of states and the resulting reaction rate constants. As already mentioned, Song & Kastner (2016) disputed the gas-phase formation of formamide through the $NH_2 + H_2CO$ reaction, arguing that the transition state connecting the van der Waals complex to the intermediate is too high when including the ZPE (from +2.7 kJ mol^{-1} to 17.8 kJ mol^{-1} with ZPE at the UCCSD(T)- F12/cc-pVTZ-F12 level of calculations) and the reaction rate coefficient very small (of the order of 10^{-22} cm^3 s^{-1}). Against this claim, it must be stressed that (i) even though the calculated energy of the transition state leading from the van der Waals complex to the bound intermediate, as results from the coupled-cluster calculations, is higher than the reactant asymptote, its energy substantially drops by including higher excitation orders in the cluster operator (see values in the previous section). Extrapolating to the full configuration interaction limit, the electronic energy of this transition state drops slightly below the reactant level (Vazart et al. 2016) in line with the variational principle of approximating from above. (ii) The use of the ZPE correction for the van der Waals complex and its transition state is not warranted. In an electronic calculation, the ZPE is derived from local considerations on the potential minimum (harmonic or anharmonic). However, the three new vibrational modes in the van der Waals complex consist of a very loose stretching mode (where even a perturbative approach including anharmonicity would tend to grossly overestimate the frequency) and two loose bending modes that constitute almost free rotations. Under these conditions, in order to derive the exact ground state level, one would have to exactly solve the Schrödinger equation on the overall potential. We believe that it is a much more realistic approach to neglect what emerges as 'the ZPE'. Taking into account the two points above, it is much more reasonable to omit the van der Waals complex from the reaction scheme rather than largely overestimate its role as done by

Table 2. Summary of the rate coefficients of the reactions involving deuterated formamide. The undeuterated case is also reported (Vazart et al. 2016). The rates are given in the usual form, $A \times (\frac{T}{300K})^{\beta} \times \exp(-\gamma/T)$. The last three columns report the values of the reaction rate at 10, 60 and 100 K, respectively, namely the temperature of a cold molecular cloud, a shocked gas (e.g. Mendoza et al. 2014) and the IRAS16293-2422 B hot corino where formamide has been detected (Jaber et al. 2014; Coutens et al. 2016).

Reaction	A ($\times 10^{-16}$cm^{3}s^{-1})	β	γ (K)	k(T = 10 K)	k(T = 60 K) ($\times 10^{-13}$cm^{3}s^{-1})	k(T = 100 K) ($\times 10^{-13}$cm^{3}s^{-1})
(1) $NH_2 + HDCO \rightarrow DCONH_2 + H$	20.7	−2.75	4.34	153	1.60	0.41
(2) $NH_2 + HDCO \rightarrow HCONH_2 + D$	1.08	−2.15	0.96	1.49	0.03	0.01
(3) $NHD + H_2CO \rightarrow$ trans-$HCONHD + H$	30.7	−2.63	5.05	141	1.93	0.52
(4) $NHD + H_2CO \rightarrow$ cis-$HCONHD + H$	26.2	−2.64	5.04	126	1.69	0.45
(5) $NH_2 + H_2CO \rightarrow HCONH_2 + H$	77.9	−2.56	4.88	287	4.41	1.23

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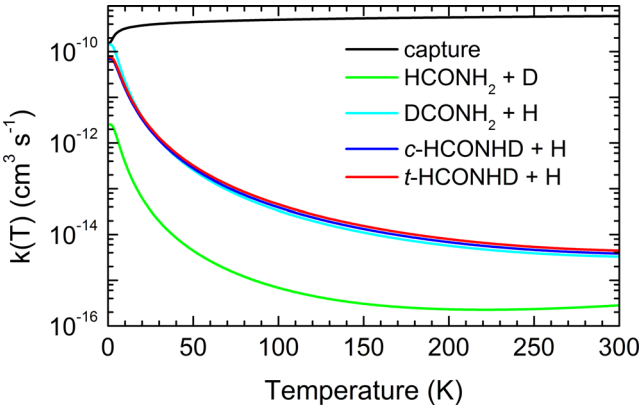

Figure 2. Canonical rate constants for the four different deuteration reactions (1)–(4) of Table 2 as a function of temperature. The capture rate constant is also shown for comparison.

Song & Kastner (2016). Kinetics experiments should be performed at very low temperatures in a Cinétique de Réaction en Ecoulement Supersonique Uniforme apparatus to verify our suggestion.

Once formed, the bound addition intermediate has two possible fates: either (a) eliminate an H/D atom and form a formamide molecule or (b) dissociate, returning to the original reactants. The relative rates of the two competing steps are important in determining overall rate constants. It is very important to stress that back-dissociation of the addition intermediate is in competition with the reactive event and its consideration in the calculations is essential to obtain meaningful rate coefficients as it reduces a lot their real values. The practice of giving the capture rate coefficient as the global rate coefficient is therefore wrong and should be avoided. Fig. 2 illustrates this point, showing the canonical rate constants for all deuteration reactions compared to the capture rate constant. It can be seen that all reaction rate constants decrease at high enough energies while the overall capture rate constant increases. This is because of the rapidly increasing back-dissociation rate, which renders simple capture rate constants completely unrealistic as estimates of reaction rate coefficients. Concerning the temperature trend, we note that at low energies (temperatures), the reaction is promoted by tunnelling while the rate of back-dissociation is negligible (as a result of the relative translation density of states tending to zero, in accordance with the detailed balance principle). As a result, reaction predominates. On the contrary, at higher temperatures back-dissociation predominates because the relative translation density of states increases more rapidly than the one of the transition state and tunnelling is no longer sufficient.

The main focus of these new calculations concerns the rate coefficients and product branching ratios of the partially deuterated species. The most relevant results can be summarized as follows: (i) the reactions involving the exit of an H atom have essentially equal rates, which are lower by a factor of 2–4 than the rate of the undeuterated reaction. For the NHD reaction, the constant capture incoming flux is split between two distinct product channels accounting for a factor of 2 (i.e. the observed difference at 10 K). The larger factor observed at higher temperatures and the reduced k(T) for the $NH_2 + HDCO \rightarrow DCONH_2 + H$ rate are, instead, direct consequences of the prevailing back-dissociation; *ii*) the reaction NH_2 + HDCO mainly produces $DCONH_2$, with only 1–2 per cent going into $HCONH_2$. The reason for this is twofold: the lighter H atom tunnels more easily through the barrier towards the products by a factor of around 50 and the vibrational ZPE of the transition state is lower when an H rather than a D atom has started dissociating.

In conclusion, even though the partially deuterated formamide products retain the degree of deuteration of the parent molecules, the three isotopic variants of the $NH_2 + H_2CO$ reactions are not characterized by the same rate coefficient. In particular, since the fastest reaction is the one with undeuterated reactants, the expected value of the degree of formamide deuteration at 100 K is a factor of 3 lower than that of the parent molecules H_2CO and NH_2.

5 COMPARISON WITH ASTRONOMICAL OBSERVATIONS AND CONCLUSIONS

So far, deuterated formamide has only been detected towards the hot corino of IRAS16293-2422 B by CJW2016. They found that the $DCONH_2/HCONH_2$ and $HCONHD/HCONH_2$ abundance ratios are similar and around 0.02–0.05. Based on this and on the fact that these ratios are smaller than the measured $HDCO/H_2CO$ abundance ratio, CJW2016 favoured a grain-surface formation of NH_2CHO. With the new computations reported in Table 2, we can now quantitatively discuss this issue. For that, we will consider the rates computed for a gas temperature of 100 K, namely the temperature in the IRAS16293-2422 B hot corino (e.g. Jaber et al. 2014).

(i) *$DCONH_2/HCONH_2$ and $HCONHD/HCONH_2$ abundance ratios smaller than $HDCO/H_2CO$.* The values in Table 2 show that there is a factor of 3 difference in the rates of formation of H- against D-formamide. Therefore, the deuteration of formamide synthesized in the gas phase will be three times smaller than that of the mother molecules NH_2 and H_2CO. No observations of NHD/NH_2 exist so far, so no constraints can be obtained from amidogen. Similarly, no observations exist of the $HDCO/H_2CO$ abundance ratio in the hot corino of IRAS16293-2422 B. However, single-dish observations of deuterated formaldehyde towards IRAS16293 measured $HDCO/H_2CO \sim 0.15$ (e.g. Ceccarelli et al. 1998; Loinard et al. 2000), namely a factor of 3–8 larger than $DCONH_2/HCONH_2$. Therefore, within the uncertainty of the available observations, the hypothesis of formamide gas formation is fully consistent with them. In addition, as correctly pointed out by CJW2016, single-dish observations encompass both the hot corino and the extended envelope. Ceccarelli et al. (2001) mapped the D_2CO line emission towards IRAS16293 and showed that the D_2CO/H_2CO abundance ratio is about 0.03. Likewise, $HDCO/H_2CO$ is also high in the extended envelope and, thus, the single-dish measurements are likely largely contaminated by the extended envelope.

(ii) *Similar $DCONH_2/HCONH_2$ and $HCONHD/HCONH_2$ abundance ratios.* The values in Table 2 show that indeed the two abundance ratios are similar (0.8–0.9) if the gaseous NHD/NH_2 and $HDCO/H_2CO$ are similar. In this respect, then, the gas-phase formation of formamide is perfectly consistent with the observed values.

We conclude that the available observations do not allow to rule out a gas-phase formation route for formamide but, on the contrary, they support it. New high spatial resolution observations of *both* NHD and HDCO towards IRAS16293 will be necessary to challenge this conclusion.

Finally, we would like to note that the same approach could be used to address the deuteration of other complex organic molecules, such as methyl formate, for which a debate on gas-phase versus ice-assisted formation routes is currently ongoing (see for instance,

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Balucani, Ceccarelli & Taquet 2015; Taquet, Wistrom & Charnely 2016).

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REFERENCES

Balucani N., Skouteris D., Leonori F., Petrucci R., Hamberg M., Geppert W. D., Casavecchia P., Rosi M., 2012, J. Phys. Chem. A, 116, 10467
Balucani N., Ceccarelli C., Taquet V., 2015, MNRAS, 449, L16
Barone V., Latouche C., Skouteris D., Vazart F., Balucani N., Ceccarelli C., Lefloch B., 2015, MNRAS, 453, L31
Caselli P., Ceccarelli C., 2012, A&AR, 20, 56
Ceccarelli C., Castets A., Loinard L., Caux E., Tielens A., 1998, A&A, 338, L43
Ceccarelli C. et al., 2001, A&A, 372, 998
Ceccarelli C. et al., 2014, in Beuther E., Klessen R. S., Dullemond C. P., Henning T., eds, Protostars and Planets VI. Univ. Arizona Press, Tucson, p. 859
Coutens A. et al., 2016, A&A, 590, L6 (CJW2016)
Dunning T. H., 1989, J. Chem. Phys., 90, 1007
Fedoseev G., Chuang K.-J., van Dishoeck E. F., Ioppolo S., Linnartz H., 2016, MNRAS, 460, 4297
Frisch M. J. et al., 2015, preprint (arXiv:e-prints)
Goerigk L., Grimme S., 2011, J. Chem. Theory Comput., 7, 291
Grimme S. J., 2006, Chem. Phys., 124, 034108
Grimme S., Ehrlich S., Goerigk L., 2011, J. Comput. Chem., 32, 1456
Jaber A., Ceccarelli C., Kahane C., Caux E., 2014, ApJ, 791, 29
Jaber Al-Edhari A. et al., 2017, A&A, 597, 40
Jones B. M., Bennett C. J., Kaiser R. I., 2011, ApJ, 734, 78
Jorgensen J. K. et al., 2016, A&A, 595, A117
Kahane C., Ceccarelli C., Faure A., Caux E., 2013, ApJ, 763, L38
Kanuchova G. et al., 2016, A&A, 585, 155
Leonori F., Skouteris D., Petrucci R., Casavecchia P., Rosi M., Balucani N., 2013, J. Chem. Phys., 138, 024311
Linsky J. L., 2007, Space Sci. Rev., 130, 367
Loinard L., Castets A., Ceccarelli C., Tielens A. G. G. M., Faure A., Caux E., Duvert G., 2000, MNRAS, 359, 1169
Lopez-Sepulcre A. et al., 2015, MNRAS, 449, 2438
Mendoza E. et al., 2014, MNRAS, 445, 151
Papajak E. et al., 2009, J. Chem. Theory Comput., 5, 1197
Parise B. et al., 2003, A&A, 410, 897
Parise B. et al., 2006, A&A, 453, 949
Raghavachari K., Trucks G. W., Pople J. A., Head-Gordon M., 1989, Chem. Phys. Lett., 157, 479.
Saladino R., Botta G., Pino S., Costanzo G., Di Mauro E., 2012, Chem. Soc. Rev., 41, 5526
Skouteris D., Manolopoulos D. E., Bian W., Werner H.-J., Lai L. H., Liu K., 1999, Science, 286, 1713
Skouteris D., Balucani N., Faginas-Lago N., Falcinelli S., Rosi M., 2015, A&A, 584, A76
Song L., Kästner J., 2016, Phys. Chem. Chem. Phys., 18, 29278
Taquet V., Wistrom E., Charnely S., 2016, ApJ, 821, 46
Vazart F., Calderini D., Skouteris D., Latouche C., Barone V., 2015a, J. Chem. Theory Comput., 11, 1165
Vazart F., Latouche C., Skouteris D., Balucani N., Barone V., 2015b, ApJ, 810, 2
Vazart F. et al., 2016, J. Chem. Theory Comput., 12, 5385

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