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# Revisiting the reactivity between HCO and CH<sub>3</sub> on interstellar grain surfaces

J. Enrique-Romero,<sup>1,2★</sup> S. Álvarez-Barcia,<sup>3</sup> F. J. Kolb,<sup>3</sup> A. Rimola,<sup>2★</sup> C. Ceccarelli<sup>1</sup>,  
N. Balucani<sup>1</sup>,<sup>1,4,5</sup> J. Meisner,<sup>3,6,7</sup> P. Ugliengo<sup>1</sup>,<sup>8</sup> T. Lamberts<sup>1</sup>,<sup>3,9</sup> and J. Kästner<sup>1</sup>,<sup>3</sup>

<sup>1</sup>Univ. Grenoble Alpes, CNRS, Institut de Planétologie et d'Astrophysique de Grenoble (IPAG), F-38000 Grenoble, France

<sup>2</sup>Departament de Química, Universitat Autònoma de Barcelona, E-08193 Bellaterra, Catalonia, Spain

<sup>3</sup>Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

<sup>4</sup>Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, Via Elce di Sotto 8, I-06123 Perugia, Italy

<sup>5</sup>Osservatorio Astrofisico di Arcetri, Largo E. Fermi 5, I-50125 Firenze, Italy

<sup>6</sup>Department of Chemistry and The PULSE Institute, Stanford University, Stanford, CA 94305, USA

<sup>7</sup>SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA

<sup>8</sup>Dipartimento di Chimica and Nanostructured Interfaces and Surfaces (NIS), Università degli Studi di Torino, Via P. Giuria 7, I-10125 Torino, Italy

<sup>9</sup>Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, NL-2300 RA Leiden, the Netherlands

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## ABSTRACT

The formation of interstellar complex organic molecules is currently thought to be dominated by the barrierless coupling between radicals on the interstellar icy grain surfaces. Previous standard density functional theory (DFT) results on the reactivity between CH<sub>3</sub> and HCO on amorphous water surfaces showed that the formation of CH<sub>4</sub> + CO by H transfer from HCO to CH<sub>3</sub> assisted by water molecules of the ice was the dominant channel. However, the adopted description of the electronic structure of the biradical (i.e. CH<sub>3</sub>/HCO) system was inadequate [without the broken-symmetry (BS) approach]. In this work, we revisit the original results by means of BS-DFT both in gas phase and with one water molecule simulating the role of the ice. Results indicate that the adoption of BS-DFT is mandatory to describe properly biradical systems. In the presence of the single water molecule, the water-assisted H transfer exhibits a high energy barrier. In contrast, CH<sub>3</sub>CHO formation is found to be barrierless. However, direct H transfer from HCO to CH<sub>3</sub> to give CO and CH<sub>4</sub> presents a very low energy barrier, hence being a potential competitive channel to the radical coupling and indicating, moreover, that the physical insights of the original work remain valid.

**Key words:** astrochemistry – molecular processes – ISM: clouds – ISM: molecules.

## 1 INTRODUCTION

Interstellar complex organic molecules (iCOMs) are usually defined as compounds of 6–13 atoms in which at least one is C (Herbst & van Dishoeck 2009; Ceccarelli et al. 2017; Herbst 2017). They are complex only from the astronomical point of view, while they are the simplest organic compounds according to terrestrial standards. Since terrestrial life is based on organic chemistry, the existence of iCOMs is of fundamental importance to ultimately understand the possible astrochemical origins of life.

iCOMs are widespread in the Universe. They have been detected in a great variety of astrophysical objects like star-forming regions (e.g. Rubin et al. 1971; Cazaux et al. 2003; Kahane et al. 2013; Mendoza et al. 2014; López-Sepulcre et al. 2015; Belloche et al.

2017; Ligterink et al. 2017; McGuire et al. 2018), in the circumstellar envelopes of AGB stars (Cernicharo, Guélin & Kahane 2000), shocked regions (Arce et al. 2008; Codella et al. 2017; Lefloch et al. 2017), and even in external galaxies (Muller et al. 2013). Despite their presence has been known for decades, how iCOMs are synthesized is still an open question and under debate (Herbst & van Dishoeck 2009; Caselli & Ceccarelli 2012; Woods et al. 2013; Balucani, Ceccarelli & Taquet 2015; Fedoseev et al. 2015; Enrique-Romero et al. 2016; Butscher et al. 2017; Gal et al. 2017; Rivilla et al. 2017; Vasyunin et al. 2017; Rimola et al. 2018; Butscher et al. 2019; Enrique-Romero et al. 2019; Lamberts et al. 2019). Two different paradigms have been proposed: (i) on the surfaces of grains (either during the cold pre-stellar or warmer collapse phase (e.g. Garrod & Herbst 2006; Woods et al. 2013; Fedoseev et al. 2015; Öberg 2016), and (ii) through reactions in the gas phase (e.g. Charnley, Tielens & Millar 1992; Balucani et al. 2015; Skouteris et al. 2018). The first paradigm assumes that whenever two radicals (e.g. created by UV photon and/or cosmic ray incidences) are in

\* E-mail: [juan.enrique-romero@univ-grenoble-alpes.fr](mailto:juan.enrique-romero@univ-grenoble-alpes.fr) (JER); [albert.rimola@uab.cat](mailto:albert.rimola@uab.cat) (AR)

close proximity (e.g. because of their diffusion) they can react to form iCOMs in a barrierless way. In the second one, iced simple hydrogenated molecules are released into the gas phase (e.g. due to thermal desorption), where they react to form iCOMs through gas-phase reactions. Interestingly, a review on the formation of iCOMs on interstellar grain surfaces investigated by means of quantum chemical calculations has recently appeared (Zamirri et al. 2019).

Currently, the ‘on-surface’ paradigm is the scheme mostly adopted in astrochemical models. However, a first theoretical study of the reactivity of HCO and CH<sub>3</sub> on an amorphous water surface (AWS), which is the bulk of the ices that envelope interstellar grains in cold objects, showed that the combination of these two radicals does not necessarily lead to the formation of the iCOM acetaldehyde (CH<sub>3</sub>CHO) (Enrique-Romero et al. 2016). This unexpected result called for and was followed by other studies of different systems and with different computational methods. First, Rimola et al. (2018) and Enrique-Romero et al. (2019) studied the formation of formamide (NH<sub>2</sub>CHO) and acetaldehyde by reactions between HCO and NH<sub>2</sub> and HCO and CH<sub>3</sub> on an AWS model by means of static quantum chemical calculations. Subsequently, Lamberts et al. (2019) studied the formation of acetaldehyde by reaction between HCO and CH<sub>3</sub> on a CO-pure ice model by means of *ab initio* molecular dynamics simulations. The three works confirmed the main finding by Enrique-Romero et al. (2016), namely that the reactivity between the radical pairs does not lead exclusively to the formation of the iCOMs, but the formation of CO + NH<sub>3</sub> and CO + CH<sub>4</sub> via direct H abstraction can also take place. In view of these results, the formation of iCOMs via the barrierless radical–radical combination scheme still needs to be validated.

In this article, we aim to revise the first calculations carried out on the CH<sub>3</sub> + HCO system (Enrique-Romero et al. 2016), which were based on the standard density functional theory (DFT) approach. Since then, it has become clear that an improved treatment of the radical spins is necessary (Rimola et al. 2018; Enrique-Romero et al. 2019). The article is organized as follows: In Section 2, we review the treatment of the spins of a biradical system, in Section 3 we provide the details of the new computations carried out in this article, in Section 4 we show the results, and in Section 5 we discuss the conclusions.

## 2 WHY A BETTER TREATMENT OF THE BIRADICAL WAVEFUNCTION IS NEEDED

In a previous work by some of us (Enrique-Romero et al. 2016), the reactivity between HCO and CH<sub>3</sub> in the gas phase and on AWS modelled by H<sub>2</sub>O ice clusters was theoretically studied with standard DFT calculations. In the gas-phase model,<sup>1</sup> different synthetic channels were identified, namely the formation of acetaldehyde (CH<sub>3</sub>CHO), CO + CH<sub>4</sub>, and CH<sub>3</sub>OCH, the occurrence of which being determined by the relative orientation of the radicals. In contrast, on the AWS models, a hydrogen-atom relay mechanism assisted by water molecules of the ice led to the exclusive formation of CO + CH<sub>4</sub>.

The electronic ground state for the CH<sub>3</sub>CHO, CO + CH<sub>4</sub>, and CH<sub>3</sub>OCH products is a singlet wavefunction as they are closed-shell systems. Conversely, the HCO and CH<sub>3</sub> radicals are open-

shell doublet systems due to their unpaired electron, while a system consisting of the two radicals (i.e. HCO and CH<sub>3</sub> together) can be either in triplet or singlet electronic states (the spins of the unpaired electrons can be of the same sign or of opposite signs, respectively). The triplet state is electronically non-reactive due to the Pauli repulsion. In contrast, the singlet state (usually referred to as a biradical system) is reactive because of the opposite spin signs. The description of the electronic structure of biradical states requires a wavefunction composed of more than one Slater determinant to recover static correlation. In the wavefunction-based post-Hartree–Fock (post-HF) realm, this can be described by multiconfigurational self-consistent field (MCSCF) methods, such as the complete active space self-consistent field (CASSCF), or the so-called multireference methods like the complete active space perturbation theory (CASPTn) ones. In CASSCF, a particular number of electrons ( $N$ ) are distributed between all possible (namely, ground and excited) configurations that can be constructed from  $M$  molecular orbitals, i.e. a  $(N, M)$  active space. It is worth mentioning that one has to pay special care when deciding the orbitals to include in the active space, since the resulting wavefunction could erroneously describe the system under study. CASPTn is an improvement over CASSCF( $N, M$ ) where a perturbative expansion is further performed in order to retrieve more dynamic electron correlation. On the other hand, such a multireference character cannot be obtained from normal Kohn–Sham DFT. Instead, the electronic structure of biradicals can be approximated by an unrestricted open-shell wavefunction with the broken-(spin)-symmetry *ansatz*, where a triplet state is mixed with a combination of ground and excited singlet states in order to obtain an electron-correlated wavefunction (Noodleman 1981; Noodleman & Baerends 1984; Neese 2004).

Calculations by Enrique-Romero et al. (2016) were performed in an open-shell formalism, but after publication we realized that the initial guess wavefunctions remained in a metastable, symmetric state with spin-up and spin-down orbitals being equally mixed (i.e. spin analysis indicated 50 per cent of spin-up and 50 per cent of spin-down in both radicals and the total spin density being zero), thus resembling a closed-shell solution. Compared to that, the actual broken-symmetry (BS) wavefunction leads to a significant stabilization of the reactants, which changes the results qualitatively. Thus, this work aims to revise some of the original results using the DFT BS solution, showing, moreover, that it agrees reasonably well with those at the CASPT2 level.

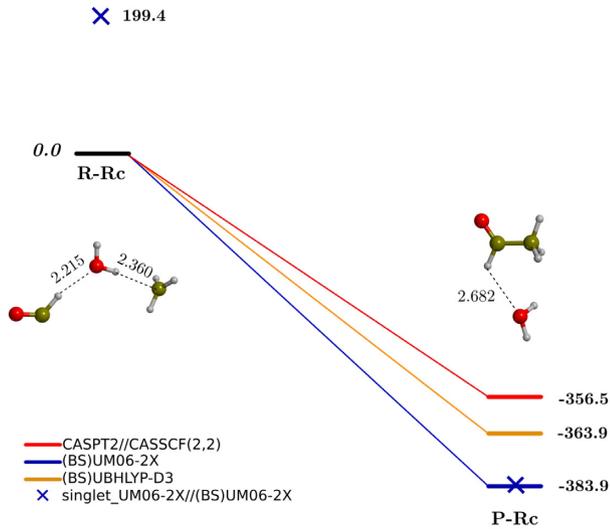
## 3 COMPUTATIONAL DETAILS

All DFT calculations were performed using the GAUSSIAN09 package (Frisch et al. 2009), while post-HF multiconfigurational and multireference calculations were carried out with the OPENMOLCAS 18.09 software (Karlström et al. 2003; Aquilante et al. 2010; Aquilante et al. 2016; Fernandez Galván et al. 2019).

DFT geometry optimizations and transition state searches were carried out with (i) the M06-2X (Zhao & Truhlar 2008) and (ii) B3LYP-D3 (i.e. B3LYP; Lee, Yang & Parr 1988; Becke 1993) including the Grimme’s D3 dispersion correction (Grimme 2006; Grimme et al. 2010) functionals, in combination with a def2-TZVPD basis set. Structures with triplet electronic states were simulated with open-shell calculations based on an unrestricted formalism. Singlet biradical systems were calculated adopting an unrestricted BS approach. For the sake of comparison, for some cases, single point energy calculations adopting standard (i.e. non-BS) unrestricted (U) formalisms have also been carried out.

<sup>1</sup>We loosely use the term ‘gas phase’ to refer to systems where no water molecule is involved. The reader has to bear in mind that these reactions cannot take place in the ISM unless a third body (i.e. the grain) absorbs the released nascent energy.





**Figure 2.** PESs at different DFT levels and at CASPT2 for the Rc reaction between  $\text{CH}_3$  and  $\text{HCO}$  in the presence of one water molecule. The 0th energy reference corresponds to the pre-reactant complex (R-Rc). Single point energies at the singlet UM06-2X level on the (BS)UM06-2X optimized geometries are also shown. The structures presented in this figure are those corresponding to the (BS)UM06-2X optimized geometries. Energy units are in  $\text{kJ mol}^{-1}$  and distances are in  $\text{Å}$ .

and a negatively charged  $\text{CH}_3$  species ( $\text{CH}_3^-$ ). This ionic state is an ideal situation to trigger a Grotthus-like mechanism, in which the ‘extra’ proton of  $\text{HCO}^+$  is transferred through the assisting water molecule to the ‘proton-defective’  $\text{CH}_3^-$ . These results confirm again the need to use the BS-DFT approach to properly describe biradical systems.

## 5 CONCLUSIONS

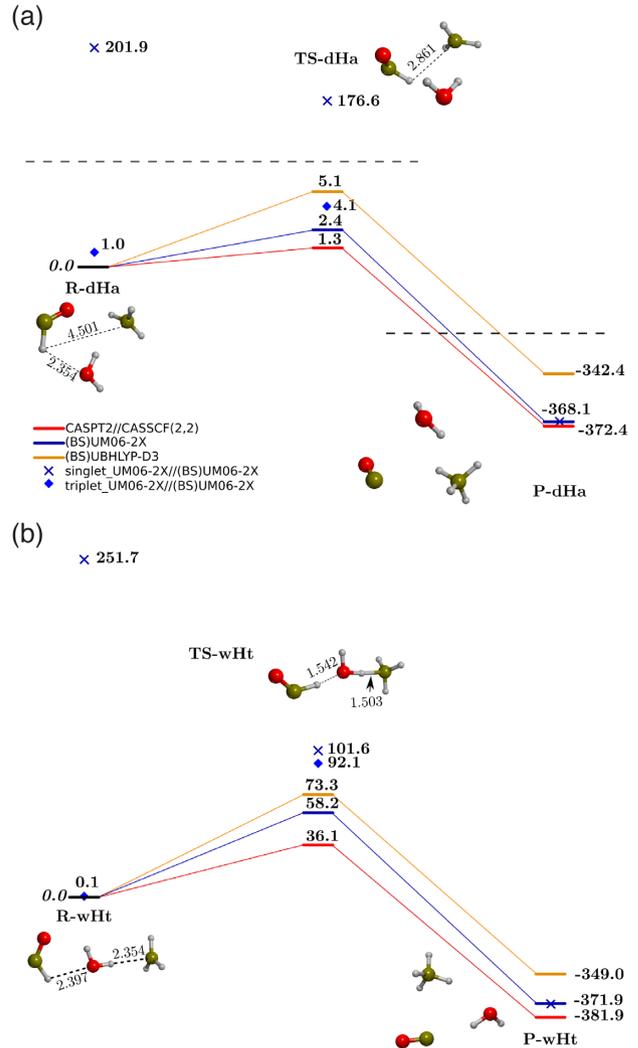
This work is a revision note of a previous work by some of us (Enrique-Romero et al. 2016), in which the reactivity of the same system, i.e.  $\text{CH}_3 + \text{HCO}$ , has been studied using DFT methods adopting an unrestricted BS approach [i.e. (BS)UM06-2X and (BS)UBHLYP-D3] as well as post-HF multiconfigurational and multireference methods [i.e. CASSCF(2,2) and CASPT2]. In the original work, the DFT BS formalism was not adopted, hence seriously affecting the description of the electronic structure of the  $\text{CH}_3/\text{HCO}$  biradical system. The main conclusions of this work are summarized as follows:

(i) When the unrestricted DFT formalism is used without adopting the BS approach to describe the electronic structure of biradical systems, the initial guess wavefunction may collapse into a restricted closed-shell solution. If this occurs, the reactivity between two radicals is likely to be wrongly described. In the particular case of the  $\text{CH}_3 + \text{HCO}$  reactivity on water ice, calculations indicate that the water-assisted H transfer process is spontaneous.

(ii) Unrestricted BS DFT calculations for biradical systems show qualitatively similar results as those obtained at post-HF multiconfigurational and multireference levels, indicating the suitability of this DFT approach to describe the reactivity of biradical systems.

(iii) In the gas phase, both  $\text{CH}_3\text{CHO}$  and  $\text{CO} + \text{CH}_4$  formations are found to be barrierless. In contrast, the formation of the carbene  $\text{CH}_3\text{OCH}$  species has a noticeable barrier.

(iv) In the presence of one water molecule, the wHt reaction is not spontaneous but, in contrast, it has a high energy [58 and 73  $\text{kJ mol}^{-1}$



**Figure 3.** PESs at different DFT levels and at CASPT2 for the reactions of dHa (a) and wHt (b) between  $\text{CH}_3$  and  $\text{HCO}$  in the presence of one water molecule. The 0th energy references are the pre-reactant complexes: R-dHa (a) and R-wHt (b). Single point energies at the singlet UM06-2X and triplet UM06-2X levels on the (BS)UM06-2X optimized geometries are also shown. The dashed horizontal lines indicate broken vertical axis. The presented structures correspond to the (BS)UM06-2X optimized geometries. Energy units are in  $\text{kJ mol}^{-1}$  and distances are in  $\text{Å}$ .

at the (BS)M06-2X and (BS)BHLYP-D3 levels]. Accordingly, its occurrence is unlikely under the interstellar conditions. In contrast, the radical–radical coupling is barrierless and the dHa presents a very small energy barrier (5  $\text{kJ mol}^{-1}$  at the most). Similar results have been obtained using larger cluster models mimicking the surface of interstellar water ice (Enrique-Romero et al. 2019).

Finally, it is worth mentioning that, despite the limited description of the biradical system in Enrique-Romero et al. (2016), the physical insights provided by that work remain still valid, since it is shown that the biradical reactivity does not necessarily result in the radical–radical coupling product (i.e. the iCOM). Indeed, it is found here that the dHa can actually be a competitive channel, giving the same product as that for the wHt. This finding is in agreement with recent theoretical works dealing with the reactivity of biradical systems on interstellar ice surfaces (Rimola et al. 2018; Enrique-Romero et al. 2019; Lamberts et al. 2019).

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## SUPPORTING INFORMATION

Supplementary data are available at *MNRAS* online.

## Appendix A.

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## APPENDIX A: ONLINE MATERIAL

In the online material file, we provide: (i) the absolute energies (in Hartrees) of the reactions presented in this work, (ii) some input examples for GAUSSAIN and OPENMOLCAS calculations, and (iii) the XYZ Cartesian coordinates of the structures presented in the work.

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