# MOLECULAR COLLISIONAL EXCITATION: THEORY, EXPERIMENT AND OBSERVATIONS

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**Abstract.**

For half a century, astrophysical molecules have been used as a proxy to understand both the chemistry and the physics of astronomical environments, from comets to star forming regions and external galaxies. In the last decade, significant progress has been made in our description of collisional excitation, thus contributing to the design of new molecular line diagnostics. In this article, we review a number of recent results in the field of molecular collisional excitation. Comparison between theory and experiment is presented for the benchmark CO molecule. We also illustrate through radiative transfer calculations that a good knowledge of (de)excitation rates allows to model strongly non-thermal spectra and to potentially detect new molecules. Finally, upcoming exciting perspectives in the field are evoked.

Keywords:    ISM: abundances, ISM: molecules, astrochemistry, molecular data, molecular processes.

## 1   Introduction

The first extraterrestrial molecule, $C_2$, was discovered in 1864 in comet Temple by Donati (1864). This was only a few years after the identification of atomic lines in the solar spectrum and well before the advent of quantum mechanics. The first interstellar molecules, CH and CN, were identified much later in the diffuse interstellar medium (ISM) (McKellar 1940). However, the realization that molecules are ubiquitous in the Universe started only in the late 1960s and early 1970s with the opening up of other wavelengths than the visible and the discovery of CO, $H_2O$, $NH_3$, etc. Microwave and infrared observations then revealed the unanticipated presence of a variety of diatomic and polyatomic molecules, molecular ions and radicals in the ISM, both in the gas-phase and on the surface of submicron-sized solid particles (dust grains). To date, more than 200 different interstellar molecules (not including isotopologues) have been detected in the gas-phase, mainly organics i.e. carbon-bearing, and containing up to 13 atoms. In addition, larger molecules with 50-100 atoms known as polycyclic aromatic hydrocarbons (PAHs) and fullerenes have been identified. Dozens of molecules are also identified in the atmospheres of cool stars, planets and comets and in proto-planetary disks. The direct analysis of carbonaceous meteorites has finally revealed that these contain an amazing variety of complex organics, including prebiotic molecules such as amino acids.

The identification of interstellar molecules entirely relies on spectroscopy. In the gas-phase, molecular lines can appear in emission or absorption, depending on the wavelength of the transition and on the physical conditions along the line of sight. The translation of the observed intensities to the molecular column density (i.e. the integration of the abundance over the line of sight) requires to understand the transport of radiation through the astronomical source. A general property of astronomical spectra is that the molecular energy level populations are rarely at local thermodynamical equilibrium (LTE). At LTE, the molecular excitation i.e. the relative number of molecules in different energy levels is described by a single temperature through the Boltzmann equation. In interstellar space, the density is usually so low that the frequency of inelastic collisons is insufficient to maintain LTE. Deviations from LTE, including strong deviations like maser phenomena, are thus very natural in star-forming regions. In these conditions, analyzing a spectrum requires to solve simultaneously the radiative transfer equation and a set of statistical equilibrium equations. Solving the statistical equilibrium in turn necessitates the avaibility of the relevant molecular data. In addition to spectroscopic parameters,

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the state-to-state rate coefficients for collisional (de)excitation by the most abundant species (H, $H_2$ and free electrons for the ISM) are of critical importance. These coefficients are extremely difficult to measure in the laboratory and astronomical models rely almost exclusively on theoretical calculations.

The present article is concerned with recent advances that have occurred in the field of molecular excitation. These studies were highly motivated by the rapid progress in astronomical instrumentation and, in particular, the recent opening of the submillimetre and far-infrared spectral domain by the Herschel Space Observatory (HSO) and the Atacama Large Millimetric Array (ALMA). The need for accurate collisional data has indeed become all the more acute with the improvements in sensitivity, spectral and angular resolution achieved with the new instruments. As we show below, similarly rapid progress has been made in molecular collision studies. In Section 2, CO is used as a benchmark molecule to illustrate the very good agreement reached between theoretical results and experimental measurements. Section 3 presents two case studies (CN and $CH_2NH$) where the knowledge of collisional data provides new chemical diagnostics. Conclusions are given in Section 4, including problems to be studied in the future.

## 2   Theory and experiment in harmony

### 2.1   Theory of molecular scattering

The quantum theory of scattering of a spherical atom by a rigid linear rotor has been formulated in the 1950s (Arthurs & Dalgarno 1960). It was however extensively developed and generalized to larger systems, including open-shell radicals, only in the 1970s and 1980s (Green 1976; Alexander & Corey 1986). Advances in this topic have been indeed closely linked with the progress in computer science. The standard scattering theory takes place within the Born-Oppenheimer approximation for the separation of electronic and nuclear motions. Scattering cross sections are obtained by solving for the motion of the nuclei on an electronic potential energy surface (PES), which is independent of the masses and spins of the nuclei. The process thus consists of two main steps. First, the electronic Schrödinger equation is solved using quantum chemistry methods for collision partners in their ground electronic states (in general). The nuclear motion is solved separately, in a second step, using quantum or (semi)classical scattering methods. A detailed description of the calculation of collisional rate coefficients from first principles can be found in the recent book edited by Lique & Faure (2019) (see Chapter 5 by Tennyson & Faure and Chapter 7 by Dagdigian).

### 2.2   The case of CO-$H_2$

For a given PES, the most exact approach is the quantum time-independent close-coupling method whose convergence can reach about 1%, depending in practice on the total number of channels involved. The accuracy of the numerous PESs for the interaction between CO and $H_2$ (the two most abundant molecules in the Universe) has been extensively checked against experiment. Comparisons include bound-states of the CO-$H_2$ complex, dissociation energies, second virial coefficients, pressure broadening parameters, state-to-state cross sections and even state-to-state rate coefficients. The different measurements are very complementary as they probe different parts of the PES. They have all confirmed that the *ab initio* coupled-cluster theory can provide an intermolecular potential accurate to about 1% in the well depth and long-range interaction regions. The latest PES for CO-$H_2$ was published by Faure et al. (2016). It was computed in full-dimensionality (6D) using the coupled-cluster method with up to perturbative quadruple excitations, CCSDT(Q), and very large basis sets.

The most sensitive scattering experiments are those at the lowest collisional energy/temperature where subtle details of the PES, especially at long-range, can lead to strong quantum effects. In this respect, cross sections in the vicinity of a rotational threshold provide very sensitive tests. Indeed sharp features in the cross sections are predicted by theory at low energy. These are referred as scattering *resonances* and they arise from purely quantum effects. Observing these resonances experimentally has remained elusive until the recent work of Michel Costes, Christian Naulin and Astrid Bergeat and their colleagues in Bordeaux (France). This group has reported the first high-resolution crossed-beam experiments on state-to-state inelastic cross sections in the cold regime using a variable crossing angle. Their experimental data are presented in Fig. 1 for the CO excitation $j = 0 \to 1$ by para-$H_2(j_2 = 0)$ (Chefdeville et al. 2015). Although the many theoretical resonances (upper panel) have been smeared out by the experimental convolution, three peaks are resolved experimentally, which are well reproduced by theory, both in position and amplitude (lower panel) (see Faure et al. (2016) for details). This very good agreement definitely confirms the high accuracy of the CO-$H_2$ PES. A review of recent

theoretical and experimental progress in molecular scattering at very low energy can be found in the book edited by Dulieu & Osterwalder (2018) (see in particular Chapters 1-3).
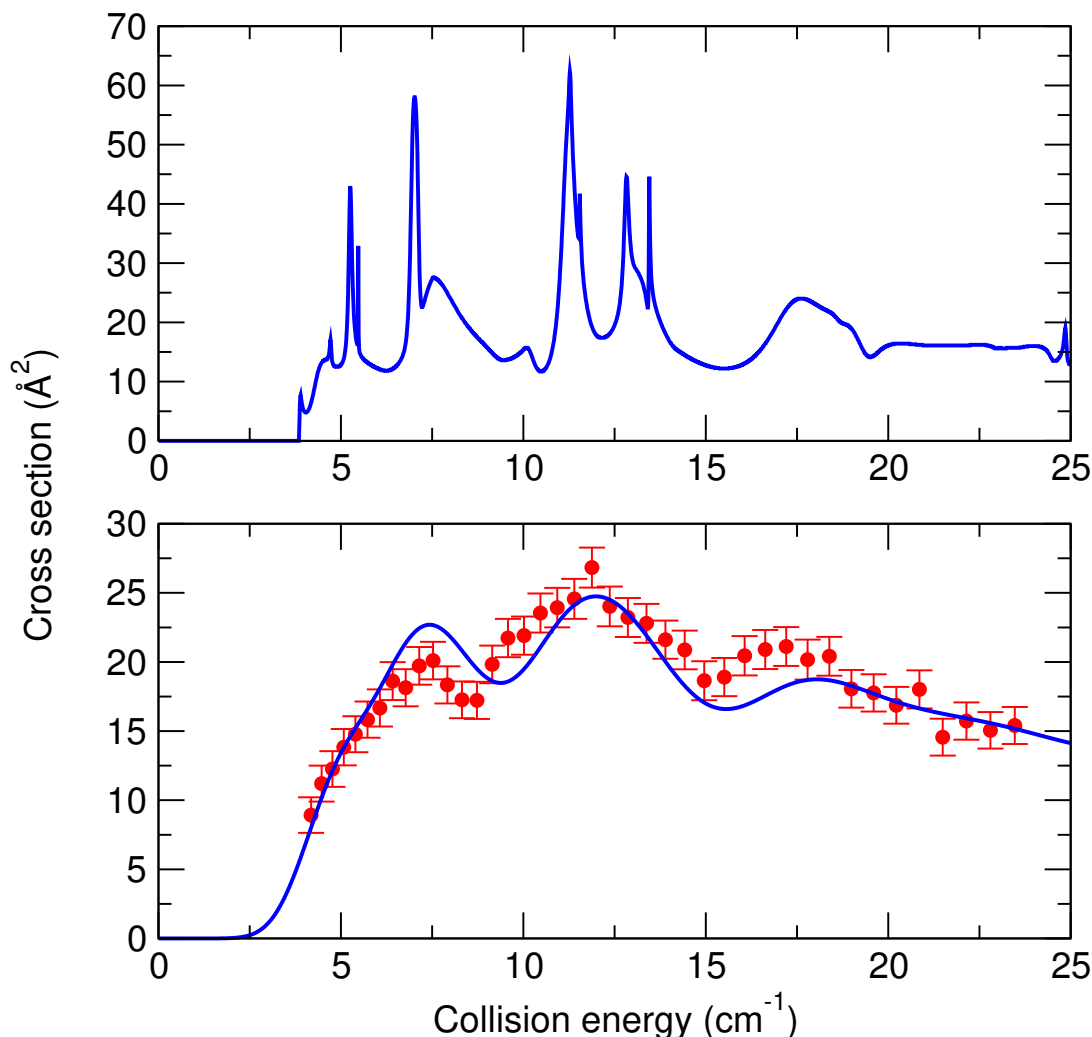


**Fig. 1.** Cross section for the CO excitation $j = 0 \to 1$ by para-$H_2(j_2 = 0)$, as function of the collisional energy. The upper panel gives the theoretical CC cross section computed with the PES of Faure et al. (2016). The lower panel gives the experimental data (red circles) and the theoretical data of the upper panel convoluted with the experimental energy spread (blue line).

## 3  Molecular excitation studies

### 3.1  The rotational excitation of interstellar CN

In diffuse interstellar clouds, where the hydrogen density is lower than $10^4$ cm$^{-3}$, the rotational temperature of optically detected molecules such as CN is generally close to that of the cosmic microwave background (CMB) radiation temperature ($T_{CMB}$=2.73 K). In the past, optical absorption-line measurements of interstellar CN have thus been used to estimate the temperature of CMB radiation at 2.6 and 1.3 mm, the wavelengths of the two lowest CN rotational transitions[*]. It was soon realized, however, that the accuracy of this indirect method was hampered by local excitation effects. Now that we know the CMB temperature with high precision,

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[*]It is instructive to note that the CMB was almost discovered in 1950 by the chemist Gerhard Herzberg who wrote about the excitation of interstellar CN that it implied "a rotational temperature of 2.3 K which has of course only a restricted meaning" (Herzberg 1950). This was 15 years before the discovery by Penzias & Wilson (1965).

$T_{\mathrm{CMB}} = 2.72548 \pm 0.00057$ K (Fixsen 2009), CN can be actually used as a probe of the local excitation. This probe however requires the knowledge of collisional rate coefficients for the rotational excitation of CN. This data has recently become available for both CN-$H_2$ (Kalugina & Lique 2015) and CN-electron (Harrison et al. 2013) collisions. The close-coupling method was employed by Kalugina & Lique (2015) while the **R**-matrix theory combined with the adiabatic-nuclei-rotation (ANR) approximation was employed by Harrison et al. (2013).

Observationally, the most recent CN optical absorption line measurements have provided a weighted mean value of $T_{01}(\mathrm{CN}) = 2.754 \pm 0.002$ K for a sample of diffuse clouds (Ritchey et al. 2011), where $T_{01}$ is the excitation temperature between the two lowest rotational levels of CN $N = 0$ and $N = 1$. This implies an excess over the CMB temperature of $T_{\mathrm{loc}} = 29 \pm 0.3$ mK. In the case of the diffuse cloud towards the star HD 154368, in addition to the optical absorption lines, the weak CN rotational emission $N = 1 \to 0$ at 2.6 mm was also detected. Since the physical conditions (hydrogen density and kinetic temperature) and the CN column density in this source are well constrained, it was possible to estimate the electron density. Thus, Harrison et al. (2013) have found that the intensity of the 2.6 mm transition could be reproduced for an electron density of $\sim 0.03$ cm$^{-3}$, corresponding to an electron fraction of $\sim 2 \times 10^{-4}$, as expected from the elemental carbon abundance ($C^+$ is the main source of electrons in diffuse clouds). We show in Fig. 2 that for this electron density, the predicted excitation temperature is $T_{01} = 2.75$ K, in very good agreement with the weighted mean value of 2.754 K determined by Ritchey et al. (2011). We finally note that this electron density is typically 3 times larger than that of the general ISM where the hydrogen density is $\sim 1$ cm$^{-3}$.
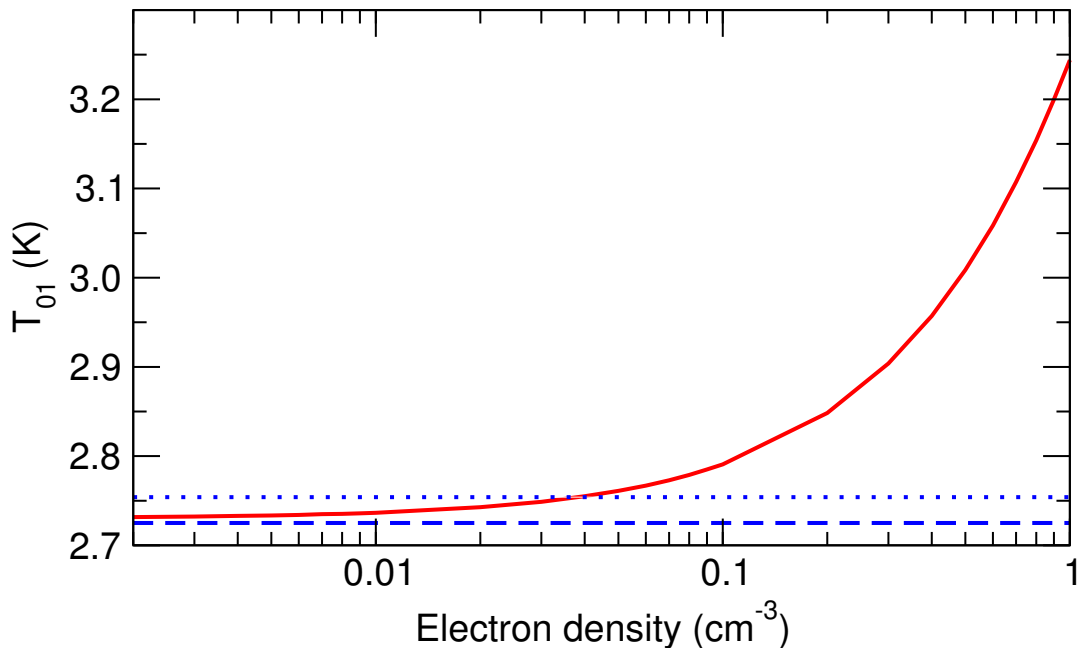


**Fig. 2.** Excitation temperature $T_{01}(\mathrm{CN})$ as a function of electron density for the physical conditions towards HD 154368 ($T$=20 K, $n$=150 cm$^{-3}$) and for a column density $N(\mathrm{CN})$=2.7×10$^{13}$ cm$^{-2}$. Here the dashed line represents the CMB at 2.725 K while the dotted blue line gives the measured average excitation temperature at 2.754 K (Ritchey et al. 2011).

### 3.2 The weak maser action of interstellar methanimine

Among the variety of interstellar organic molecules, imines are of special interest because they are possible precursors of amino acids. Amino acids are the building blocks of proteins and the study of simpler precursors in space may help to decipher the origin of life on Earth and elsewhere in the Universe. Methanimine ($CH_2NH$), the simplest imine, was discovered in the ISM in 1973 towards the giant molecular cloud Sgr B2 *via* the hyperfine multiplet structure of the $1_{10} \to 1_{11}$ rotational line at 5.29 GHz (Godfrey et al. 1973). Since then, $CH_2NH$ has been detected in many galactic and even extragalactic sources from centimetric to millimetric wavelengths. In order to elucidate the chemistry of $CH_2NH$ in the ISM, it is important to derive reliable column densities and therefore to perform non-LTE radiative transfer calculations. In particular, the strong emission of the intrinsically weak $1_{10} \to 1_{11}$ line towards Sgr B2 was soon attributed to a population inversion, rather than an

anomalously high abundance. The knowledge of collisional data, however, was missing until recently.

The first rotational rate coefficients for $CH_2NH$ were determined by Faure et al. (2018) by combining an *ab initio* $CH_2NH-H_2$ PES with close-coupling scattering calculations. Moreover, new observations were performed towards Sgr B2(N) (the north core of Sgr B2) with the Green Bank Telescope (GBT). The multiplet of the 5.29 GHz line was detected with a high signal-to-noise ratio, as shown in Fig. 3. It should be noted that two velocity components are resolved in this spectrum, which correspond to two different molecular clouds lying surimposed along the same line of sight, in front of the strong continuum emission produced by Sgr B2(N). Radiative transfer calculations were performed with the non-LTE RADEX program (van der Tak et al. 2007). The kinetic temperature and density of $H_2$ for both molecular clouds were fixed at $T=30$ K and $n_{H_2} = 10^4$ cm$^3$, respectively, as derived by Faure et al. (2014) from their modeling of the weak $HCOOCH_3$ masers. The column density of $CH_2NH$ was adjusted for each cloud to best fit the observational spectrum. Other details can be found in Faure et al. (2018). A very good agreement between the observation and the model is observed in Fig. 3. As anticipated, the $1_{10} \rightarrow 1_{11}$ line was found to be inverted with an excitation temperature of -0.48 K. This inversion, by amplifying the strong background continuum radiation, is thus critical here to produce the emission of the otherwise undetectable 5.29 GHz multiplet. As a result, searching for maser lines could be very fruitful to detect new chemical species with intrinsically low abundance.
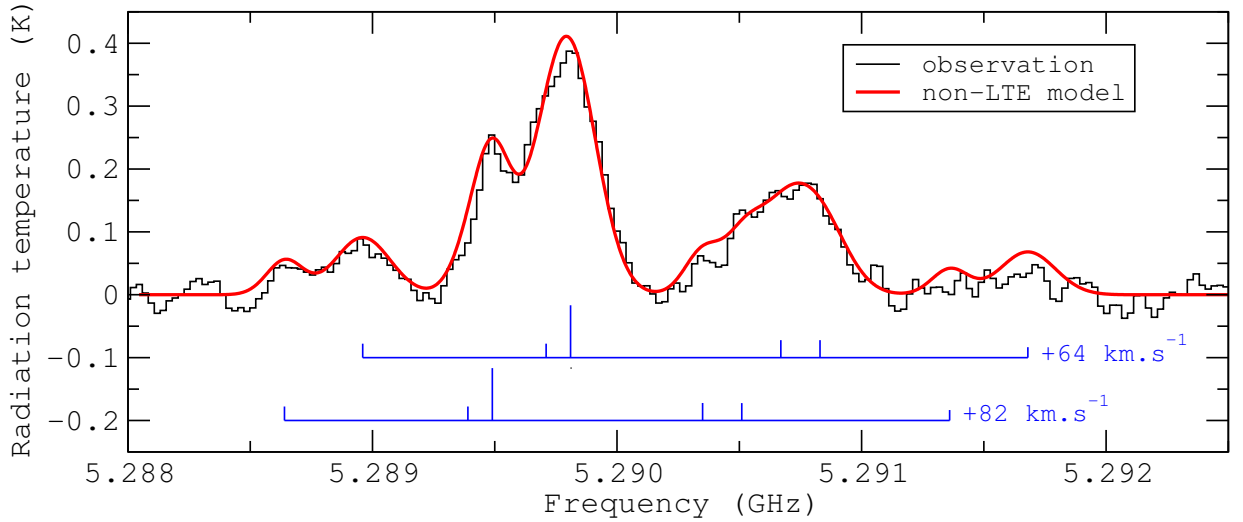


**Fig. 3.** Observational and model spectra of methanimine $1_{10} \rightarrow 1_{11}$ transition at 5.29 GHz towards Sgr B2(N). Relative intensities of the (partially resolved) hyperfine structure in the optically thin limit are shown at the bottom. The nominal source velocity is +64 km.s$^{-1}$. A second velocity component is resolved at +82 km.s$^{-1}$. The non-LTE model predicts a population inversion with a negative excitation temperature $T_{ex} = -0.48$ K.

## 4 Conclusions

Recent years have seen impressive theoretical and experimental progress regarding the description of inelastic molecular collisions involving small, non-reactive and vibrationally cold molecules. Thus, current theoretical data for rotational excitation can reach a precision of $\sim$ 10-20% that fully matches the astrophysical requirements for the modelling of both rotational spectra and cooling. This has remarkably contributed to improve the diagnostic power of rotational lines. The next step is to extend the current level of accuracy *i)* to large molecules, *ii)* to ro-vibrational excitation and *iii)* to other projectiles such as $H_2O$ or CO (important in comets and planetesimals). Recent examples include the work by Faure et al. (2019), Stoecklin et al. (2019) and Loreau et al. (2018), respectively. Another requirement concerns *reactive* species which are both excited and destroyed by H, $H_2$ or free electrons. A recent example can be found in Faure et al. (2017) for the molecular ion $CH^+$. Guided by the enhanced sensitivity of new telescopes (JWST, E-ELT, etc.) and the prospect to detect molecular lines from Earth-like exoplanets and the early Universe, we are confident that the study of molecular collisional excitation has a bright future.

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