

MOLECULES AS A DIAGNOSTIC TOOL IN ASTROPHYSICS

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Abstract. In a first part, this paper focuses on collisional excitation rates of molecules by He and H₂ relevant to the interstellar medium. It discusses currently available data and outlines new work carried out by the team of authors. The new rate coefficients differ significantly from previously published ones. In a second part, the paper analyzes from some examples how the use of the new rates could lead to important changes in the interpretation of molecular emission emerging from molecular clouds.

1 Introduction

Over the next few years, ground-based and space-based missions will open up the universe to high spatial and spectral resolution studies at infrared and submillimeter wavelengths. This will allow to study, in much greater detail, the composition and the origin and evolution of molecules in space. These new missions can be expected to lead to the detection of many thousands of new spectral features. Identification, analysis and interpretation of these features in terms of the physical and chemical characteristics of the astronomical sources will require detailed astronomical tools supported by

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laboratory measurements and theoretical studies of chemical reactions and of collisional excitation rates on species of astrophysical relevance.

The present paper focuses in a first part on recent theoretical studies on collisional excitation rate coefficients of molecules by He and H₂: these processes are important as they contribute to molecular excitation in competition with radiative processes. In cold environments such as the interstellar medium, collisions with H₂ are the most important because of its high abundance and collisions with He are often considered as a model for collisions with H₂. In a second part, we analyse the impact of these new rate coefficients on astrophysical modeling in comparison with previous data. All the published rate coefficients can be found on the BASECOL database (<http://www.obspm.fr/basecol>) by Dubernet et al. (2005).

2 Collisional excitation rates in the ISM

Within the Born Oppenheimer approximation the determination of these collisional rate coefficients requires two steps: the calculation of the interaction between nuclei and electrons for fixed nuclei, leading to the so-called potential energy surface (PES) and the scattering calculations. In the context of observations in the mm and submm ranges, the collisions concern regions with relatively low temperatures ($5\text{K} < T < 1000\text{K}$), there is no electronic excitation and no reactive channels and the collisions generally involve a limited number of PES describing a van der Waals system.

Recent progress in *ab initio* quantum chemistry permit very accurate determinations of the PES of small non-reactive systems. For inter-molecule PES, the coupled cluster theory with singles, doubles and perturbative triples (CCSD(T)) is generally assumed to be very accurate as long as only one configuration contributes to the electronic state. Various techniques can be used to approximate the infinite basis set limit at the CCSD(T) level of theory. A popular approach is to associate bond functions in order to improve the description of the wavefunction between the interacting molecules. An alternative method is to describe properly the electron-electron correlation which is responsible of the slow convergence of the conventional approaches with respect to the basis set size. In particular the so-called CCSD(T)-R12 approach is computationally practical and proved highly accurate, in particular using adequate R12-suited basis sets (Faure et al. 2005).

Quantum close-coupling (CC) scattering calculations are feasible in the low energy range and lead to nearly exact results. Calculations can be extended to higher energies using approximate quantum or semi classical approaches. The fast and popular Infinite Order Sudden (IOS) quantum approximation usually converges well whenever the relevant Δj energies are small in comparison to the available collisional energy. When the energy is augmented this condition is fulfilled for the lower j levels, but not for the highest j levels. In that respect the extension of the present scattering calculations to the obtention of inelastic rates for warm gas or shocked regions may be problematic if accurate results are sought.

2.1 $N_2H^+ + He$

Up until now the only available rate coefficients were pure rotational rate coefficients among rotational levels $j < 6$ and for temperatures up to 40K. They were calculated by Green (1975) using an electron gas model for the PES. Using an adiabatic decoupling approximation a two-dimensional PES corrected for the influence of the ν_1 stretching vibration was calculated by Meuwly et al. (1997) at the CCSD(T) level using the aug-cc-pVQZ atomic orbital basis set. The percentage difference between earlier rotational results by Green (1975) and new calculations by Daniel et al. (2005) are larger for transitions with large Δj and vary in the range from a few percent to 100%. Overall the new rates are larger for all transitions and the differences decrease with increasing temperatures.

In astrophysical applications the splittings due to couplings with the nuclear spins of the two nitrogen atoms are resolved and there are 9 hyperfine components for a given rotational level $j > 1$. The cross sections between hyperfine levels are obtained using a recoupling technique, first introduced by Corey & McCourt (1983) for the case of a single electronic spin and extended in Daniel et al. (2004) to the case of 2 nuclear spins. The dynamical problem is solved using close coupling methods. It is found that the only well defined propensity rule among hyperfine rate coefficients is $\Delta F = \Delta F_1 = \Delta j$ and that calculations are required in order to obtain the relative intensities of the 2 spin hyperfine rate coefficients at temperatures below 50 K. Daniel et al. (2005) note that the usual simple approaches such as IOS scaling and proportionality of the hyperfine rate coefficients to the final degeneracy of the hyperfine levels are inadequate at low energies. The $N_2H^+-H_2$ system is currently under investigation.

2.2 *SO + He*

The previous available rate coefficients were provided by Green (1994) for the SO-H₂ system at temperatures ranging from 50K to 350K. The author used a CS-H₂ PES adapted from an electron gas model of CS-He. The rate coefficients among fine levels were obtained with a IOS scaling relationship (Neufeld et al. 1994). New collisional excitation cross sections of the fine levels of SO have been recently calculated by Lique et al. (2005a) at low energies using a full close-coupling (CC) treatment and a new ab initio PES calculated at the CCSD(T) level using the aug-cc-pVQZ atomic orbital basis set complemented by bond functions. Rate coefficients were obtained for temperatures ranging from 5K to 50K. The results displayed the expected propensity rule $\Delta j = \Delta N$. The use of recoupling techniques from spin-free cross sections was investigated at low energy. This approximation is not valid for excitation between the first levels ($N \leq 5$) where the fine structure splitting is large compared to the rotational splitting but it provides reasonable estimate of rates for high-J levels at large temperatures.

Rate coefficients have been obtained for higher temperatures (50K < T < 300K) from the same PES. Full-CC calculations were performed for the first levels ($N \leq 5$). The rates among higher levels were obtained using an “hybrid” technique combining full CC calculations at low energies, IOS scaling relationship from pure rotational cross sections for intermediate energies and pure IOS calculations for high energies (Lique et al. 2005b). The expected accuracy of the rates, compared to a full CC calculation, varies from 5% for the first levels to 20-30% for the higher levels. Calculations for ro-vibrational excitation of SO are in progress.

2.3 *CS + He*

Previously, calculations were done for CS-H₂ by Green & Chapman (1978) and extended by Turner et al. (1992) using a PES adapted from an electron gas model for CS-He and the coupled states approach. New scattering calculations were performed recently by Lique et al. (2005c) using full CC approach. An accurate ab initio PES was calculated at the CCSD(T) level using the aug-cc-pVQZ atomic orbital basis set complemented by bond functions. Comparison was made with the results of Turner et al. (1992) by transforming their CS-H₂ rate coefficients into CS-He rate coefficients by a ratio of the reduced mass of the different systems. The comparison

shows a relatively good agreement for transitions with low Δj and low j ($j \leq 3$), even if the difference increases with the temperature and can be as high as a factor 2. However large difference factors (up to 3-4) may exist for transitions with large Δj . The comparison shows that the differences are mainly due to the different PES used.

2.4 $H_2O + H_2$

The available excitation rate coefficients are those calculated by Phillips et al. (1995, 1996) using the close-coupling and the coupled states methods with the PES calculated by Phillips et al. (1994). Data were provided between 20K and 140K for a number of ortho/para H_2O -ortho/para H_2 pure rotational transitions. These calculations were extended to 5K (Dubernet et al. 2002, Grosjean et al. 2003) using pure CC calculations and the same PES. The results presented in Dubernet et al. (2002) are significantly different from those presented earlier, in particular the excitation rate for the $1_{01} - 1_{10}$ transition is more than 50% larger than in Phillips et al. (1996). This is a consequence of an unsufficiently fine energy grid used by Phillips et al. (1996) in integrating the cross-sections over the Maxwellian distribution of kinetic energies.

A new accurate 9D PES of the $H_2O + H_2$ system was recently calculated by Faure et al. (2005a) using a procedure combining CCSD(T) and CCSD(T)-R12 methods. A 5D PES was also obtained by averaging the 9D PES over the ground vibrational states of H_2O and H_2 . Using this averaged 5D PES new scattering calculations were carried out for the excitation of H_2O (000) by H_2 ($v=0$) with a large basis set as reported in Daniel et al. (2006a). The rates involving ortho- H_2 are changed by 10 to 20% only, while low energy para- H_2 rates may differ by a factor of 2 or more.

3 Astrophysical implication

It is important to know the impact of these new rate coefficients on astrophysical modeling, in comparison with the use of the previous ones. Considering N_2H^+ , the rotational excitation of this molecular ion was recently studied. LVG (Large Velocity Gradient) and non-local models were computed in order to interpret the hyperfine lines observed with the 30m-IRAM telescope in a set of 15 dark clouds (Daniel et al. 2006b). Using a LVG

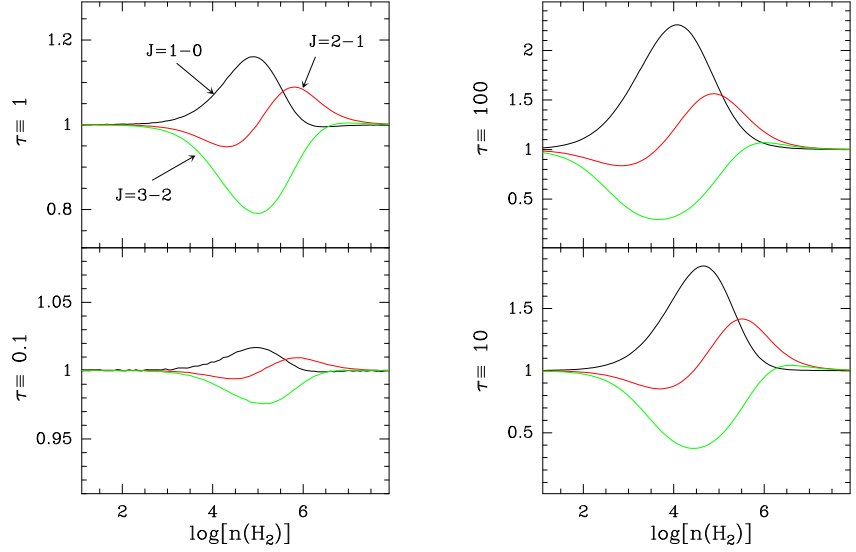


Fig. 1. Ratio between the opacities of the 3-2, 2-1 and 1-0 rotational lines of N_2H^+ , R_τ , obtained with and without hyperfine description. The column density has been set to obtain opacities of the 1-0 around 0.1, 1, 10 and 100. The column densities are $\simeq 2.2 \cdot 10^{11}$, $2.3 \cdot 10^{12}$, $2.5 \cdot 10^{13}$ and $2.4 \cdot 10^{14} \text{ cm}^{-2}$ respectively.

code, it was shown that the opacities and excitation temperatures of the rotational lines obtained with the two sets of rates (Daniel et al. 2005, Green 1975) agree within 20%. However, the LVG model used in the comparison treats independently the transitions among the hyperfine levels and does not account for local overlap. LVG calculations of the emerging flux were performed with and without hyperfine structure using the corresponding hyperfine or rotational sets of rates. Figure 1 shows the ratio of the summed hyperfine opacities versus the rotational opacities for total opacities in the 0-1 line ranging from 0.1 to 100. From this comparison, it is found that the total opacities, obtained for the rotational lines by summation of the opacities of the hyperfine lines over all the possible initial and final levels, are not identical in the two approaches. The discrepancies occur in a range of densities around the critical densities, the effect increases with the total opacity of the lines. This result points out the necessity to take into ac-

count explicitly the exact hyperfine structure of the levels in the modeling of N_2H^+ . Furthermore, if the ETL approximation is used, additional errors will be made on the estimated opacities of the hyperfine components as they are thought to be proportional to the total opacity of the rotational line weighted by the line strength of each component.

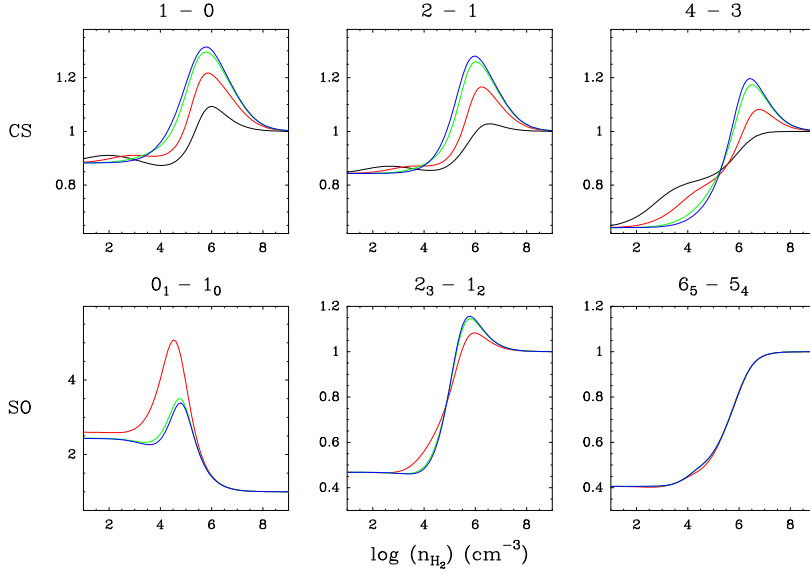


Fig. 2. Comparison of brightness temperatures calculated using new rates and previous ones. On all the graphs, the H_2 density varies between 10 and 10^9 cm^{-3} . 2a, upper panel : Brightness temperature ratios (T_B (Turner et al. 1992 rates) / T_B (Lique et al. 2005c rates)) for the 1-0, 2-1 and 4-3 lines of CS. The CS column density varies from $3 \cdot 10^{12}$ to $3 \cdot 10^{15} \text{ cm}^{-2}$ by step factors of 10 (blue, green, red and black lines respectively). 2b, lower panel : Brightness temperature ratios (T_B (Green, 1994 rates) / T_B (Lique et al. 2005a rates)) for the $0_1 - 1_0$, $2_3 - 1_2$ and $6_5 - 5_4$ lines of SO. The SO column density varies from $3 \cdot 10^{12}$ to $3 \cdot 10^{14} \text{ cm}^{-2}$ by step factors of 10 (blue, green and red lines respectively).

The effect of the new rates on the excitation of SO and CS has been studied by modeling this excitation through a LVG radiative transfer code.

Figure 2a shows the comparison between the results obtained for CS with our rate coefficients and those of Turner et al. (1992) for a temperature of 150K and CS column densities ranging from $3 \cdot 10^{12}$ to $3 \cdot 10^{15} \text{ cm}^{-2}$ by step factors of 10. The brightness temperature ratio T_B , for the 1-0, 2-1 and 4-3 lines exhibits differences as large as 20-30 % for these lines. This result is not surprising and reflects the difference between the two sets of rates. Our rates for high temperatures and high j are always above those of Turner et al. (1992). The use of the latter rates could lead to important errors in the interpretation of CS molecular emission emerging from warm molecular clouds and high mass star forming regions.

The same study was performed for the excitation of SO. We have compared (Lique et al. 2006) the brightness temperatures T_B at $T_K = 20\text{K}$ obtained for recently observed SO lines by using the rates of Lique et al. (2005a) and those of Green (1994). The corresponding ratio is plotted in Fig. 2b as function of the H_2 density for SO column densities ranging from $3 \cdot 10^{12}$ to $3 \cdot 10^{14} \text{ cm}^{-2}$ by step factors of 10. We can see that the differences are important especially for the $0_1 - 1_0$ transition. As a consequence, interpretation of dark molecular clouds based on the observation of this transition can lead to a very important underestimation (up to a factor 10) of the H_2 density if the rates of Green (1994) are used.

From these few examples, it appears clearly that reliable astrophysical modeling needs accurate molecular data and in particular accurate collisional rate coefficients if the ETL is not realized. This will be of a particularly great importance for the interpretation of the data that extremely powerful instruments such as Herschel and ALMA will provide in the next years.

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