

MOLECULAR EXCITATION BY INELASTIC COLLISIONS

L. Wiesenfeld¹, A. Faure¹, N. Troscompt¹, P. Valiron¹, N. Crimier and C. Ceccarelli¹

Abstract. Interstellar clouds are mainly composed of hydrogen molecules whose molecular spectra are difficult to record. Major other components are polar molecules, whose rotational and ro-vibrational spectra are readily observed. Inelastic collisions of molecules with H₂ and electrons are important processes to understand the formation and intensities of molecular spectral lines. We present an overview of recent calculations performed in Grenoble, as part of the European Union FP6 program MOLECULAR UNIVERSE milestones.

1 Introduction

A notable fraction of the ordinary matter mass of the galaxy is contained in various kinds of gaseous or granular interstellar matter (ISM). Interstellar matter form vast clouds that fall into different categories, but they all share some features: low to extremely low densities, from 10³ part./cm³ to 10¹⁰ part./cm³, low temperatures (10 K ≤ T ≤ 300 K). Overall, ISM comprises molecular and atomic gases, some ionized matter and grains of various compositions, which are covered with ices at low temperatures. Still, its dominant component is hydrogen (in the form mainly of H₂, except where strong UV radiation is important). Among all tools that astrophysics has to probe interstellar matter, molecular rotational spectroscopy is particularly valuable. Spectral lines of polar molecules are readily observed in the cm to sub-mm bands, corresponding mainly to various kinds of rotational or ro-vibrational transitions of polar molecules. A general and up-to-date introduction to ISM and its spectral properties may be found in Tielens (2005).

In order to understand the spectra that we observe, two kinds of questions must be answered: i. Why is the species that I record observed in the particular object I am interested in ? ii. What is the line profile, including absorption/emission and intensity, of the various spectral transitions that I may record? Answering question (i.) is a matter of astrochemistry. Models of chemistry depend on the one hand on the kinetics and thermodynamics of the hundreds of chemical reactions that proceed simultaneously in a typical ISM cloud and on the other hand on the physical conditions of the ISM under study. A recent review is Herbst (2005). Answering question (ii.) requires the knowledge of two different pieces of information. On the macroscopic side, one has to know how the photon emitted by the source either the background source or the molecule itself is transmitted through the ISM in order to reach the antenna. In order to answer this question, we need a model of radiative transfer. Many such models exist, relying on various approximations, from the simplest ones, where the state of the gas is supposed to be in a steady state, homogeneous and optically thin to the most sophisticated, allowing for even superradiance (maser) effects, see Elitzur, 1992. The other part of the question is microscopic: What is the excitation/deexcitation scheme of the molecule; is it excited via collisions with hydrogen molecules, electrons or photons?

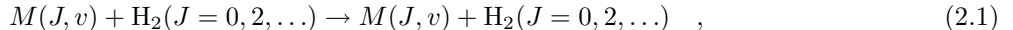
We present in this short overview some recent work that we have undertaken in order to answer the very last question. The next section presents a general theoretical scheme that allows for the calculation of inelastic cross-sections and rates. Afterwards, we list some noticeable recent results of our team.

¹ Laboratoire d'Astrophysique, UMR 5571 CNRS, Université Joseph-Fourier, B.P. 53, 38041 Grenoble cedex 09, France

2 Molecular Collisions

2.1 Critical densities

As alluded to in the previous section, the different rotational levels of a molecule M may be populated by inelastic collisions with other molecules. Since H_2 is by far the most probable collision partner, molecule M undergoes in effect two types of collisions at low temperatures, either with para- H_2 :



or else with ortho- H_2 , where H_2 remains in $J = 1, 3, \dots$. In order to know the populations $M(J, v)$, we need to calculate either cross sections $\sigma_{JJ'}(E)$ (E being the collisional energy) or the collision rate at temperature T , being defined as (μ , reduced mass):

$$k_{J,J'}(T) = \left[\frac{8}{\pi\mu (kT)^3} \right]^{1/2} \int \sigma_{JJ'}(E) \exp(-E/kT) E \, dE \quad (2.2)$$

The knowledge of the excitation rates $k_{JJ}(T)$ allows one to define a critical density n_J^* , for the level J . It is defined as the density of collisional partner, $n(\text{H}_2)$, at which collisions are as important as spontaneous emission (Goldsmith 1972). The critical density may be defined as:

$$n_J^* = \frac{\sum_{J'} A_{JJ'}}{\sum_{J'} k_{JJ'}(T)} \quad (2.3)$$

where the sum is over all reachable states J' and $A_{JJ'}$ is the spontaneous emission Einstein coefficient. It is often considered that for $n(\text{H}_2) \gg n_J^*$, for all J levels considered, molecule M is at the so-called Local Thermodynamical Equilibrium, its rotational temperature being that of the kinetic temperature. At lower densities, as mentioned earlier, more or less elaborate models must be used in conjunction with the values of $k_{JJ}(T)$. A good knowledge of $k_{JJ}(T)$ is thus a necessary prerequisite for the precise determination of the physical conditions of the ISM. The calculation of $k_{JJ'}(T)$ goes into two parts, namely a potential part and a dynamical part. The first part of the calculation amounts to determine the Potential Energy Surface (PES) between molecule M and H_2 . Since molecule M does not react with hydrogen nor does any hydrogen exchange occur in our systems, the interaction $M - \text{H}_2$ is a typical van der Waals complex, where the interaction energy is very weak. In all cases that have been calculated, binding energies are of the order of a few hundreds of wave-numbers. It is thus necessary to calculate the interaction between the two molecules with great care, all the more that each individual total molecular energy amounts to several tens of eV. References may be found in Noga et al. (1994) and Kedzuch et al. (2005).

2.2 Dynamics

From the knowledge of the PES, we are able to undertake the second part of the program, namely a collision calculation. For quantum dynamics it is customary to solve the close-coupling equations. This is usually performed with help of an existing code. Our choice went to the MOLSCAT code; see all technical details in Hutson (1994), Dubernet et al., (2002, 2003). The limitations on most quantum calculations come from the size of the matrices to be multiplied or inverted. While purely quantum calculations are feasible for rigid-body water and for rigid-body like cyanoacetylene, up to $J \sim 15$, they become impractical or downright unfeasible if vibrations are included or if the number of channels to be included becomes too large. There exist various quantum approximations to the full close-coupling calculation, that neglect various coupling terms, thereby reducing the sizes of the matrices to be dealt with. These are the so-called Infinite Order Sudden approximation (IOS) and Coupled States approximation. Their validity for the problem and energy at hand must each time be carefully validated; IOS calculations are particularly suitable if the energy differences between the various channels is tiny with respect to the collision energy. That is why it has been used for collisions dealing with hyperfine levels. An alternate and very useful route is to use quasi-classical trajectories (QCT), with initial conditions that fulfill quantization conditions and a final analysis with help of a binning method (Faure et al. 2005), . This route is particularly suited for high energy collisions, where a quantum formalism leads to expensive calculations while the system may approach classical limits, despite some limitations in the treatment of quantum symmetries.

2.3 Electron Molecule Collisions

Despite low electron fraction in the ISM (about 10^{-4} in diffuse clouds and much smaller in dense clouds), electron collisions are very efficient in rotationally exciting molecules. This is because rate coefficients for electron-impact excitation are typically 4-5 orders of magnitude greater than the corresponding rates for neutral excitations. Among different theoretical techniques for treating electron-molecule collisions, the molecular R-matrix method is one of the most successful. The basic idea of the R-matrix method is the division of coordinate space into two regions, an inner region bounded by a sphere and an outer region. The inner region is designed to enclose the entire N-electron target wave-function. The outer region is so chosen that for scattering problems it is only necessary to consider some simplified long-range, multipolar, interaction. The R-matrix is the mathematical tool designed to communicate the necessary information between the two regions. Electron-correlation effects are included in the target wavefunctions via configuration interaction expansions. R-matrix calculations have shown that simple long-range approximations (e.g. Coulomb-Born) are not reliable for computing rate coefficients and that rotational transitions with $\Delta J > 1$, which are neglected in a pure dipolar approximation, do have significant cross sections. These calculations have been also demonstrated to give an accuracy rivaling, and sometimes exceeding experiment. Present results for astronomical applications include H_2^+ , HeH^+ , CH^+ , CO^+ , NO^+ , HCO^+ , H_3^+ , H_3O^+ , H_2O , HCN , HNC and deuterated isotopologs. A fuller account is given in an accompanying paper by Faure et al. in these proceedings.

3 Grenoble case studies

3.1 Potential energy surfaces

Mainly in the framework of the FP6 "Molecular Universe" program, a certain number of potential energy surfaces have been calculated in the Grenoble group. They are summarized in table 1.

Table 1. Potential energy surfaces calculated for inelastic scattering purposes

System	Comments	Reference
$\text{H}_2\text{O} - \text{H}_2$	Equilibrium Geometry, High precision	a
$\text{H}_2\text{O} - \text{H}_2$	Full nine-dimensional surface	b
$\text{HC}_3\text{N} - \text{H}_2$	Vibrationally averaged geometry	c
$\text{HC}_3\text{N} - \text{He}$	Vibrationally averaged geometry	c
$\text{NH}_3 - \text{H}_2$	Vibrationally averaged geometry	d
$\text{NH}_3 - \text{He}$	Vibrationally averaged geometry, including inversion	d
$\text{H}_2\text{CO} - \text{H}_2$	Vibrationally averaged geometry	d
$\text{H}_2\text{CO} - \text{He}$	Vibrationally averaged geometry	d

Ref: (a): P. Valiron, A. Faure, C. Rist, unpublished work. (b) : A. Faure, P. Valiron, M. Wernli, L. Wiesenfeld, C. Rist, J. Noga, J. Tennyson, 2005 Journal of Chemical Physics **122** 221102; (c) M. Wernli, L. Wiesenfeld, A. Faure, P. Valiron; 2007 Astronomy and Astrophysics **464** 1147; (d) P. Valiron, unpublished results.

Examples of PES are shown in figure 1. Some comments are in order. A first question that arises when calculating a Potential Energy Surface (PES) that is non reactive: Which geometry do we use for the two scattering partners. A standard answer used to be 'Equilibrium geometries', that is, geometry at the minimum of the isolated molecules PES. For example, this amounts for the H_2 molecule to a $r_{\text{HH}} = 1.400 \text{ \AA}$. The first $\text{H}_2\text{O} - \text{H}_2$ PES, ref (a) in table 1, was calculated this way. The other extreme way is to calculate the PES leaving all degrees of freedom active, that is, allowing for the interatomic distance to vary slightly around their equilibrium values. We undertook such a calculation for the same system, $\text{H}_2\text{O} - \text{H}_2$ (ref (b) of table 1). This type of PES allows several interesting applications:

1. Calculate the rates of vibrational excitation (here the H_2O bending mode) by the incoming H_2 collider, see Faure et al. (2005).

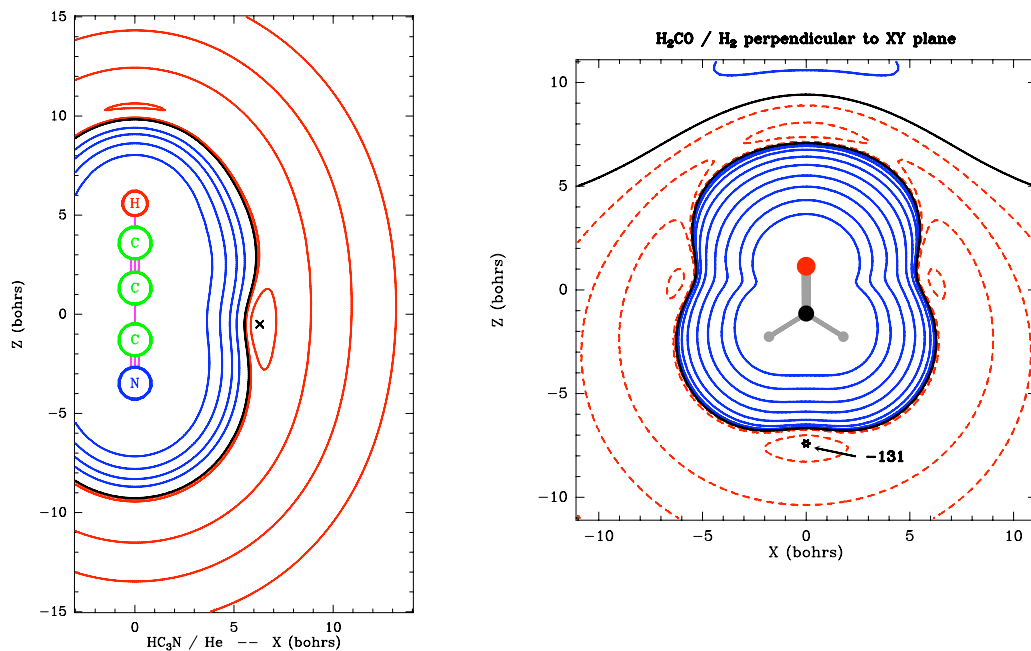


Fig. 1. Potential energy surfaces for the $\text{HC}_3\text{N} - \text{He}$ interaction (left) and the $\text{H}_2\text{CO} - \text{H}_2$ interaction (right). Repulsive part in blue, zero line in black, attractive part in red. HC_3N from Wernli et al. 2007., H_2CO , P. Valiron, unpublished results.

2. Calculate, in an adiabatic way, the effect of the approaching collider on the geometry of the other molecule, hence, on the cross section.
3. Determine which average geometry reproduces best the effects of point 2 above.

Clearly, if vibrational motion is purely harmonic, at second order, the vibrationally averaged structure (called usually the r_0 structure) and equilibrium structure (the r_e structure) coincide. Taking into account the anharmonicities changes the r_0 structure with respect to the r_e one. For the H_2 molecule this is an important effect, which amounts to varying from $r_e(\text{HH}) = 1.400 \text{ \AA}$ to $r_0(\text{HH}) = 1.449 \text{ \AA}$. Similarly, the OH distance in H_2O goes from 1.809 \AA to 1.843 \AA . All subsequent PES calculations were performed using *vibrationally averaged* structures; In practice, only bonds and angles involving H atoms are affected by this averaging procedure. All quantum chemical details pertaining the PES calculations may be found in Kedzuch et al. (2005) or in Wernli et al. (2006). For H_2CO , see Troscompt et al. (2007).

3.2 Cross-sections and rates

We have described in an earlier part (see section 2.2) all the methods recently employed in Grenoble to calculate cross section and rates of rotational (de)excitation of molecules through collisions with He atoms and H_2 molecules, in the para (J even) or ortho (J odd) states. Similarly to section 3.1 above, let us put forward some of our recent published achievements:

As a first example, we list in Table 2, the critical densities obtained for the various levels of H_2O , with comparison from earlier work. Data are taken from Faure et al. (2007).

There are many applications to the knowledge of these rates. One obvious application is the calculation of line intensities, using these rates in some photon propagation code. Several types of approximation exist, among which the LVG (Large Velocity Gradient) is widely used. We made use of this approximation to examine the importance of these new rates for the H_2O and H_2CO observations. In particular, the new, high-quality

Table 2. Recent rates calculated in Grenoble, for molecular excitation purposes

System	Temperature range for rates (K)	Method	Comments	References: PES; dynamics
CO – H ₂	5 – 70	High-precision calculations	Close coupling	(a),(aa)
H ₂ O – H ₂	300 – 4000	Vibrational excitation	Quasi-classical	(b);(b)
H ₂ O – H ₂	–	Ro-vibrational excitation	Methodology	(b);(ab)
H ₂ O – H ₂	20 – 2000	Rotational excitation	Quasi-classical	(b);(ac)
HC ₃ N – H ₂	5 – 100	Rotational excitation	Quantum and classical	(c);(c)
H ₂ CO – H ₂	5 – 100	Rotational excitation	Quantum	(d);(ad)

Ref: (a): P. Valiron, A. Faure, C. Rist, unpublished work. (b) : A. Faure, P. Valiron et al, 2005. (c) M. Wernli et al., 2007.(d) P. Valiron, unpublished results. Faure, A.; Crimier, N. et al., 2007. (aa) Wernli et al., 2006; (ab) Faure and Wiesenfeld, 2004; (ac) Faure, Wiesenfeld, et al. 2006; Troscompt et al., in preparation, 2007

Table 3. Critical densities, in cm⁻³, for (scaled) He, para-H₂ and ortho-H₂, as functions of temperature and for a set of representative H₂O levels. Powers of 10 are given in parentheses. See text for details.

$J_{K_a K_c}$	$T(K)$	He	p-H ₂	o-H ₂	He/p-H ₂	He/o-H ₂
1 ₁₀	100	1.3(08)	6.3(07)	3.0(07)	2.1	4.3
	300	5.7(07)	3.6(07)	2.5(07)	1.6	2.3
	1000	3.0(07)	2.3(07)	2.2(07)	1.3	1.4
3 ₁₃	100	3.2(09)	1.1(09)	7.0(08)	2.9	4.6
	300	1.6(09)	7.7(08)	5.6(08)	2.1	2.9
	1000	8.4(08)	5.1(08)	4.5(08)	1.6	1.9
4 ₁₄	100	6.6(09)	2.5(09)	1.4(09)	2.6	4.7
	300	3.2(09)	1.5(09)	1.1(09)	2.1	2.9
	1000	1.5(09)	9.3(08)	8.2(08)	1.6	1.8
5 ₁₅	100	1.2(10)	4.8(09)	2.6(09)	2.5	4.6
	300	5.8(09)	2.9(09)	1.9(09)	2.0	3.1
	1000	2.5(09)	1.6(09)	1.4(09)	1.6	1.8
6 ₁₆	100	2.3(10)	8.6(09)	4.2(09)	2.7	5.5
	300	1.0(10)	4.9(09)	3.1(09)	2.0	3.2
	1000	4.1(09)	2.5(09)	2.1(09)	1.6	2.0
10 ₂₉	100	2.0(11)	4.0(10)	9.8(09)	5.0	20.4
	300	6.9(10)	1.9(10)	8.1(09)	3.6	8.5
	1000	2.0(10)	8.5(09)	6.3(09)	2.4	3.2

excitation rates change the predicted line intensities for the Herschel lines of water by as much as a factor 10. As a second example, let us compare an excitation rate for the H₂CO – H₂ collision, our calculations for both ortho-H₂ and para-H₂ and S. Green calculation of 1991 (Fig. 2). We see that a new PES allowed for (i) a clear difference between p-H₂ and o-H₂ and (ii) an important rescaling with the older calculation of S. Green, due probably to the large dipole-induced dipole and dipole quadrupole interactions between formaldehyde and hydrogen molecules.

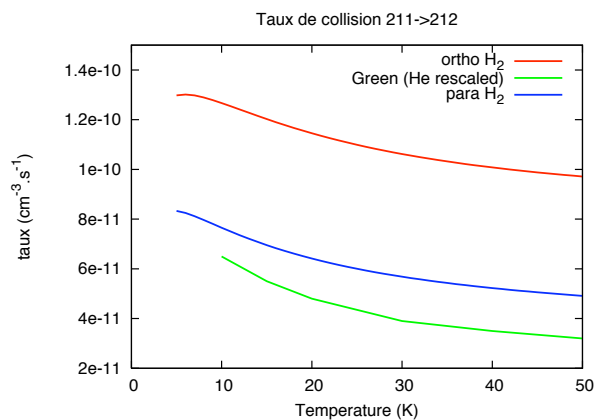


Fig. 2. Potential energy surfaces for the $\text{HC}_3\text{N} - \text{He}$ interaction (left) and the $\text{H}_2\text{CO} - \text{H}_2$ interaction (right). Repulsive part in blue, zero line in black, attractive part in red, Troscompt et al, 2007.

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