

Collisional Excitation Rates in the ISM

M. L. Dubernet¹, P. Valiron³, F. Daniel¹, A. Grosjean²,
F. Lique¹, N. Feautrier¹, A. Spielfiedel¹, A. Faure³,
M. Wernli³, L. Wiesenfeld³, and C. Rist³

¹LERMA, UMR CNRS 8112, Paris Observatory, 5 Place Janssen, 92195 Meudon, France
email: marie-lise.dubernet@obspm.fr

²LAOB, Observatoire de Besançon, UMR CNRS 6091, Université de Franche-Comté,
41 bis avenue de l'Observatoire, BP 1615, 25010 Besançon Cedex, France

³Laboratoire d'Astrophysique de Grenoble, UMR 5571 CNRS-UJF, OSUG,
Université Joseph Fourier, BP 53, F-38041 Grenoble Cedex 9, France

Abstract. The paper focuses on collisional excitation rates of molecules by He and H₂ relevant to the interstellar medium. It discusses currently available data, presents very recent work and outlines new work being carried out by various teams.

Keywords. ISM: molecules — molecular data — molecular processes

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

The present paper focuses on the latest theoretical studies on collisional excitation rate coefficients for molecules colliding with H₂ and He; 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 most important because of its high abundance, and collisions with He are often considered as a model for collisions with H₂.

All the published rate coefficients used in astrophysical applications can be found on personal websites, such as those of S. Green (<http://www.giss.nasa.gov/data/mcrates/>) and D. Flower (<http://ccp7.dur.ac.uk/>) and in recent compilations, such as the Leiden Atomic and Molecular Database LAMDA (<http://www.strw.leidenuniv.nl/~moldata/>) by Schröier *et al.* (2005) and the BASECOL database (<http://www.obspm.fr/basecol>) by Dubernet *et al.* (2005). Those recent compilations have different approaches. The LAMDA database contains ready-to-use rate coefficients of the rotational excitation of molecules by H₂ with extrapolations of rate coefficients in temperature and in transition, and connections of those rate coefficients to spectroscopic data from the JPL and CDMS catalogues. The BASECOL database contains all published rate coefficients and gives a complete information on the origin of the data with all relevant references. All

the information given in the present paper on previous calculations is collected from the BASECOL database. The BASECOL database is a continuously evolving service that will offer standardized tools for manipulating fundamental rate coefficients and spectroscopic data and that will be included in the future theoretical services of the Virtual Observatory.

2. Methodology

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 so-called potential energy surfaces (PESs) and the scattering calculations. In the context of observations in the mm and submm range, the collisions concern regions with relatively low temperatures ($5 \text{ K} < T < 1000 \text{ K}$), there is no electronic excitation, nor any reactive channels, and the collisions generally involve a limited number of PESs describing a van der Waals system : a single PES for Σ states and two surfaces for Π states.

2.1. Potential Energy Surfaces

Recent progress in *ab-initio* quantum chemistry permits very accurate determinations of the PESs of small non-reactive systems. As the complexity of the calculations increases very steeply with the target accuracy, significant savings can be obtained using hierarchies of basis sets, correlation methods and meshes. By combining advanced treatments of both the electronic correlation and nuclear motion, a typical cm^{-1} accuracy can be achieved for intra-molecular PESs, as demonstrated by Polyansky *et al.* (2003) and Rajamaki *et al.* (2004) for vibrational investigations of H_2O and NH_3 .

For inter-molecular PESs involving non-reactive molecules the coupled cluster theory with singles, doubles and perturbative triples, CCSD(T), is generally assumed to be very accurate. However, the effects resulting from theoretical levels beyond CCSD(T) are poorly known for such systems. From a comparison to experimental virial coefficients Jankowski & Szalewicz (2005) estimated they might amount to several cm^{-1} in the vicinity of the CO-H_2 minimum. Basis set superposition errors are sizeable even for the largest basis set sizes, and should be removed by counterpoise. 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 to large augmented correlation basis sets in order to improve the description of the wavefunction between the interacting molecules. This approach may be complemented with basis set extrapolation, as in Jankowski & Szalewicz (2005) and references therein.

An alternative method is to describe properly the electron-electron correlation cusp that is responsible for the slow convergence of all conventional approaches with respect to the basis set size. Such explicitly correlated methods offer a direct way of reaching the basis set limit values within a single calculation, i.e. without extrapolation. In particular the so-called CCSD(T)-R12 approach is computationally practical and proven to be highly accurate, in particular using adequate R12-suited basis sets. Appropriate references can be found in Faure *et al.* (2005a). Such CCSD(T)-R12 calculations can also be used to monitor the accuracy of conventional PESs, as was done for He and H_2 interacting with CO, NH_3 , HF and HC_3N in Wernli *et al.* (2005), Valiron (unpublished) and Wernli *et al.* (2006).

2.2. Scattering Calculations

Quantum close-coupling 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. For vibrational quenching or excitation rates, the corresponding VCC-IOS approximation may also prove questionable for molecule-molecule pairs involving large rotational constants, as pointed out by Krems *et al.* (2001) and Faure *et al.* (2005b). In that respect the extension of present scattering calculations to the obtaining of inelastic rates for warm gas or shocked regions may be problematic, if accurate results are sought.

3. New Results

3.1. $H_2O + H_2$

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

A new 9D PES of the H_2 – H_2O system has recently been calculated by Faure *et al.* (2005a) using a three-step procedure: (i) a 5D rigid-rotor PES reference was computed at the CCSD(T) level of theory; (ii) this reference surface was then calibrated to few cm^{-1} accuracy using 812 “high cost” CCSD(T)-R12 calculations; (iii) the R12-corrected rigid rotor surface was then extended to 9D using a new set of CCSD(T) calculations. The resulting 9D PES contains all relevant information to describe the interaction of all H_2O – H_2 isotopomers in zero-point or excited bending states. As a first application, high temperature ($1500 < T < 4000$ K) rate constants for the relaxation of the ν_2 bending mode of H_2O were estimated from quasiclassical trajectory calculations by Faure *et al.* (2005a) and the role of rotation in the vibrational relaxation of water is emphasized by Faure *et al.* (2005b). Their results are larger by an order of magnitude than those currently used in the astrophysical literature and might lead to a thorough reinterpretation of vibrationally excited water emission spectra from space.

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 rotational excitation of $H_2O(000)$ by $H_2(v=0)$ using the same procedure as in Dubernet *et al.* (2002) and Grosjean *et al.* (2003) with a larger basis set as reported in Daniel *et al.* (2006). 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.

These changes reflect the improvements in the PES, where surprisingly the largest contribution is attributed to the vibrational averaging. However Valiron *et al.* (2006a)

showed that the vibrationally averaged PES can be accurately approximated by rigid rotor calculations using properly vibrationally averaged geometries for both interacting molecules, as already postulated by Mas & Szalewicz (1996) and Jeziorska *et al.* (2000). This simplification may facilitate accurate PES calculations whenever inelastic vibrational effects are not to be considered. An application is underway for $\text{H}_2\text{CO}-\text{H}_2$ by Valiron (2006b).

3.2. $\text{N}_2\text{H}^+ + \text{He}$

Up until now, the only available rate coefficients for N_2H^+ excited by He were pure rotational excitation rate coefficients among rotational levels $j < 6$ and for temperature up to 40 K. There were calculated by Green (1975), using an electron gas model for the potential energy surface. Using an adiabatic decoupling approximation a two-dimensional potential energy surface corrected for the influence of the ν_1 (mainly NH-local mode) stretching vibration was calculated by Meuwly & Bemish (1997) at the CCSD(T)/aug-cc-pVQZ level. Its reliability has been assessed by comparing energies of bound states and rotational constants with experimental data (Meuwly *et al.* 1996). The percentage differences 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%. In overall the new rates are larger for all transitions and the differences decrease with increasing temperature.

In astrophysical applications only 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 $j > 0$. 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 reduces to spin-less equations, which is solved using close-coupling (CC) 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 temperature below 50 K. Daniel *et al.* (2005) note that the usual simple approaches such as Infinite Order Sudden scaling and proportionality of the hyperfine rate coefficients to the final degeneracy of the hyperfine levels are inadequate. The authors provide Boltzmann averages of the so-called opacity factors; these allow calculation of pure rotational rate coefficients, rate coefficients among hyperfine levels as well as among magnetic sublevels of hyperfine levels for the 7 first rotational levels and for temperature less than 50 K.

These new results have been used in astrophysical applications (Daniel *et al.* 2005; Daniel *et al.* 2006a) and scattering calculations are currently extended to reach a temperature of 300 K. The $\text{N}_2\text{H}^+ + \text{H}_2$ system is currently under investigation by M. Meuwly and M.L. Dubernet.

3.3. $\text{SO} + \text{He}$

The previous available rate coefficients were provided for the $\text{SO}-\text{H}_2$ system by Green (1994) at temperatures ranging from 50 K to 350 K among the 70 lowest fine-structure energy levels corresponding to a maximal rotational level $N_{max} = 23$. The author used a $\text{CS}-\text{H}_2$ PES, which had been adapted (Green 1975) from an electron gas model (Gordon *et al.* 1972) of $\text{CS}-\text{He}$, treating the CS molecule as a rigid rotor. The long range part of the $\text{CS}-\text{He}$ PES had been modified to account for the electrostatic interaction between CS and H_2 . The rate coefficients among fine-structure levels were obtained with an IOS scaling relationship similar to the one used by Neufeld & Green (1994) for $\text{HCl} + \text{He}$.

New collisional excitation cross sections of the fine-structure levels of SO colliding with He have recently been calculated by Lique *et al.* (2005a) at low energies using a full close-coupling treatment and a new ab initio potential energy surface calculated at the CCSD(T) level with an aug-cc-pVQZ basis set complemented by bond functions. Rate coefficients were obtained for temperatures ranging from 5 K to 50 K. The results displayed the expected propensity rules $\Delta J = \Delta N$. 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 where the fine structure splitting is large compared to the rotational splitting, but it should provide a reasonable estimate of rates for high- J levels at large temperatures. Some preliminary tests by Lique *et al.* (2005b) show that the use of the new rate coefficients compared to the use of rate coefficients previously calculated by Green (1994) can significantly change the diagnostics of the SO abundance in dark clouds. Calculations for temperatures up to 300 K are under way.

3.4. $HC_3N + He/H_2$

The currently available rate coefficients are those of Green & Chapman (1978); they are calculated among the 21 lowest rotational levels for $T = 10, 20, 40, 80$ K using quasiclassical calculations combined with the Infinite Order scaling relationship. Their PES is computed with an electron gas model PES (Gordon *et al.* 1972), treating the HC_3N molecule as a linear rigid rotor, with bonds fixed at experimental values.

Two new PESs have been calculated at a CCSD(T) level for the HC_3N -He and HC_3N - H_2 systems by Wernli *et al.* (2006). The new HC_3N -He agrees pretty well with the PES obtained by Akin-Ojo *et al.* (2003). Steric hindrance problems involving the HC_3N rod limit the convergence of the angular expansion of the PES, as anticipated by Green & Chapman (1978). However for low energy collisions Wernli *et al.* (2006) showed it is feasible to regularize the PES by smoothing out the repulsive walls and to achieve a perfectly converged angular expansion. Corresponding close-coupling calculations led to surprising results due to the rod-like features of the PES. Firstly quantum interferences strongly disfavour odd Δj transitions and favour even Δj ones. This propensity rule is likely to favour the $J = 1$ population for H_2 densities in the 10^3 - 10^4 cm^{-3} range. Secondly, despite the very large HC_3N dipole moment, the para- H_2 and ortho- H_2 rates are nearly identical. While the even Δj propensity rule could not be found in the quasiclassical calculations by Green & Chapman (1978), the new rates remain within the same order of magnitude despite the very crude electron gas model PES. This is not too surprising as the rod-like features of the PES dominate the scattering.

3.5. $CO + H_2$

Rotational rate coefficients among the lowest 29 levels of CO with para- H_2 ($j = 0$) and the lowest 20 levels of CO with ortho- H_2 ($j = 1$) were provided using the close-coupling method by Flower (2001) for temperatures ranging from 5 K to 400 K. Those calculations were of better quality and superseded the results of Mengel *et al.* (2001). It should be noted that both Flower and Mengel used the PES of Jankowski & Szalewicz (1998), but Mengel used a scaled version of the PES, while Flower used it without modifications. Quantum mechanical studies of this system had previously been undertaken by Green & Thaddeus (1976), who used a scaled CO-He interaction PES, and by Flower & Launay (1985) and Schinke *et al.* (1985), who used a different ab initio CO- H_2 PES.

The Jankowski & Szalewicz (1998) PES has recently been improved by Jankowski & Szalewicz (2005) and new close-coupling calculations were carried out for the rotational excitation of CO by H_2 (see Wernli *et al.* 2005). The authors confirmed the quality of the PES by independent CCSD(T)-R12 calculations, and found that a 10% difference

in the PES brings about a 30% to 50% difference in the final rate coefficients at low temperature compared to the earlier results by Flower (2001). They also reported fair agreement above a temperature of 70 K.

3.6. $NH_3 + He$

Numerous studies have been carried out on the rotational excitation of NH_3 . The available set of data concerns the rotational excitation of NH_3 by He, obtained by Green (1981) using coupled states calculations and a PES of Davis *et al.* (1979).

A new set has been calculated by Machin & Roueff (2005) using rigid-body close-coupling calculations (no inversion) with a PES by Hodges & Wheatley (2001). They report de-excitation rate coefficients for transitions up to $j = 4$ for para- NH_3 , and up to $j = 7$ for ortho- NH_3 for temperatures between 5 K and 300 K. Large differences are obtained with the previous results of Green (1981), mainly attributed to the PES changes. Comparisons with experiments fare well when the rate coefficients are summed over the 2 final parity components. It is believed that the discrepancies with experimental results come from the neglect of the inversion motion.

Interaction energies were checked against CCSD(T)-R12 calculations by Valiron (unpublished) for several interacting geometries and intermolecular separations. The PES by Hodges & Wheatley (2001) is slightly too repulsive. Agreement is better along the attractive orientations, with a 2 cm^{-1} offset for the absolute minimum, and poorer for the less attractive orientations with a typical 5 cm^{-1} offset at 7 bohrs, to be compared to the $\sim 35\text{ cm}^{-1}$ absolute minimum. As the scattering is expected to be most sensitive to the minima and to the positioning of the repulsive walls this surface should provide a fair accuracy for astrophysical applications. PES and rate calculations involving the dominant collision partner H_2 are planned within the Molecular Universe European network.

3.7. $HF + He$

Various studies have been carried out on ro-vibrational excitation of HF by He. The latest study involves the calculation of a new PES by Stoecklin *et al.* (2003) at a CCSD(T) level with an aug-cc-pVQZ basis set complemented by bond functions. Interaction energies for both the primary and secondary minima were checked against CCSD(T)-R12 calculations by Valiron (unpublished) and agreed to within 0.3 cm^{-1} . This extremely accurate PES by Stoecklin *et al.* (2003) was subsequently used for close-coupling calculations of the rotational excitation of HF by Reese *et al.* (2005). The authors provide rotational de-excitation rate coefficients for levels up to $j = 9$ and for temperatures up to 300 K. It should be noted that Moszynski *et al.* (1994) and Moszynski *et al.* (1996) had provided a SAPT PES that agreed well with a semi-empirical PES of Lovejoy & Nesbitt (1990) obtained from near-infrared spectroscopy.

The predicted rates are small and lead to a high critical density, in agreement with the modeling of the pioneering HF_{2-1} observations in absorption towards Sgr-B2 by Neufeld *et al.* (1997). However due to the large dipole moment of HF the collisional rates with ortho- H_2 might be substantially higher.

4. Conclusions

Accurate predictions of collisional excitation rates are now feasible for a large set of small-molecule interactions with He and H_2 .

The accuracy of the potential energy surfaces (PES) can be monitored at a given level of theory using basis set extrapolation techniques or preferably by explicitly correlated approaches, and few cm^{-1} accuracy is now attainable for small non-reactive molecules.

Ideally, the PES should be averaged over the relevant vibrational states of both interacting molecules. However it is sufficient to perform rigid rotor calculations using vibrationally averaged geometries. Recent investigations using new PESs for CO, H₂O, NH₃, N₂H⁺, SO and HC₃N permitted the estimation of the influence of PES errors on the final inelastic rates. Except at very low temperature or for the smallest rates the error amplification is moderate, generally much below an order of magnitude. Consequently accurate PESs with a few cm⁻¹ accuracy should lead to 5–10% accuracy in the rates if appropriately converged and energy-averaged close-coupling calculations can be performed. However that level of PES accuracy is highly computer-time consuming. It requires an optimized choice of the grid geometries for the ab initio calculations and performance of an analytic fit of the PES leading to some additional inaccuracy.

Moreover the best level of accuracy is out of reach of current approximate approaches for scattering. Accordingly, the main source of uncertainties may come in the future from the scattering calculations instead of the PES, especially for higher energies or inelastic ro-vibrational rates for which brute force close-coupling calculations are not feasible, especially as mixing between electronic states may occur.

On the other hand, astronomers are welcome to express their needs in terms of accuracy, as much cheaper PESs would be sufficient to obtain moderate rate accuracies.

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Discussion

TOWNES: Are there any experimental results, which directly test your calculations of cross-sections, and if so how well do they agree?

DUBERNET: No there are, unfortunately, no direct experimental tests as yet.