

Collisional excitation of complex organic molecules

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Abstract. A major difficulty in modelling the infrared and (sub)millimeter spectra of gas-phase complex organic molecules is the lack of state-to-state collisional rate coefficients. Accurate quantum or classical scattering calculations for large polyatomic species are indeed computationally highly challenging, particularly when both rotation and low frequency vibrations such as bending and torsional modes are involved. We briefly present here an approximate approach to estimate and/or extrapolate rotational and rovibrational rates for polyatomic molecules with many degrees of freedom.

Keywords. Molecular data, molecular processes, ISM: molecules

1. Introduction

In the past few years, observations of star forming regions have revealed unexpected high abundances of complex organic molecules such as ketene (H_2CCO), methyl formate (HCOOCH_3), dimethyl ether (CH_3OCH_3), etc. (e.g. Ceccarelli *et al.* 2007). The detailed modelling of these observations is however currently hampered by the lack of state-to-state collisional rates. A major problem relates to the fact that quantum scattering calculations for such complex species are impractical owing to the excessively large number of coupled channels to be included in the solution of the Schrödinger equation. Moreover, classical mechanics has other severe intrinsic limitations (e.g. Faure & Wiesenfeld 2004). As a result, the largest system for which absolute rovibrational state-to-state cross sections are available is E-type methanol colliding with He (Pottage *et al.* 2004a).

2. Rotational excitation and the information theory

The information theory was introduced in the early 1970's as a procedure to compact and correlate the large amounts of data, both theoretical and experimental, on molecular collisions (Levine 1978 and references therein). In this approach the decrease of (de)excitation rates with increasing inelasticity is described through purely statistical factors and an exponential gap law. Despite its simplicity, this theory was shown to properly account for the underlying qualitative trends of energy transfer processes. Based on this theory, we have derived a simple analytic formula to describe pure rotational rate coefficients. This formula, supplemented with collisional propensity rules, has been calibrated and checked against the accurate quantum calculations of Pottage *et al.* (2004b) for E-type methanol. The results are presented in Figure 1.

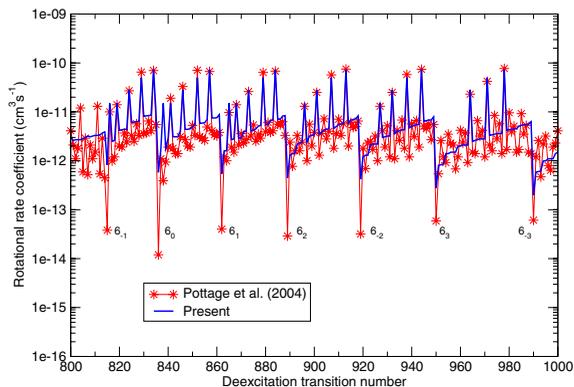


Figure 1. Sample of rotational rates for E-type methanol colliding with para-H₂ at 100 K. The present calculations are based on an exponential gap law supplemented with the quantum propensity rules $\Delta K = 0, \Delta J < 6$. The agreement with the results of Pottage *et al.* (2004b) is typically within a factor of 3, except for very low rates.

3. Rovibrational excitation and critical densities

There is to our knowledge no state-to-state rate coefficients available for rovibrational processes involving polyatomic molecules. Based on data available in the literature, however, it appears that these rates can be assumed, *to first order*, to be proportional to the pure rotational rates. We have derived a formula where the proportionality coefficient *i*) is calibrated over theoretical or experimental data, *ii*) is defined so that rates obey the detailed balance principle and *iii*) depends on temperature. For example, for the torsional mode of E-type methanol, this coefficient is about 10^{-2} at 700 K (Pottage *et al.* 2004a).

If we now consider the critical densities of rovibrational levels of complex molecules, we can summarize the situation as follows:

- For levels in the ground vibrational state, critical densities are typically $n < 10^5 \text{ cm}^{-3}$. Non-LTE rotational populations are expected in regions with density $n < 10^7 \text{ cm}^{-3}$.
- For levels in excited vibrational states, critical densities are $n > 10^9 \text{ cm}^{-3}$. Non-LTE vibrational populations are expected in, e.g., circumstellar envelopes with density $10^7 < n < 10^{11} \text{ cm}^{-3}$.

4. Conclusion

The present method allows to estimate and/or extrapolate collisional rates for complex organic molecules, including possibly vibrational modes. It should provide guidance at the order-of-magnitude level. It is also expected to become more accurate at high temperatures ($> 300 \text{ K}$) where standard quantum methods are impractical. More details and examples will be published elsewhere.

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