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The rotational excitation of HCN and HNC by He: temperature dependence of the collisional rate coefficients

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ABSTRACT

Modelling of molecular emission from interstellar clouds requires the calculation of rates for excitation by collisions with the most abundant species. This paper deals with the calculation of rate coefficients for rotational excitation of the HCN and HNC molecules in their ground vibrational state in collision with He. Calculations of pure rotational (de-)excitation cross-sections of HCN and HNC by He were performed using the essentially exact close-coupling method. Cross-sections for transitions among the 26 first rotational levels of HCN and HNC were calculated for energies up to 3500 cm^{-1}. These cross-sections were used to determine collisional rate constants for temperatures ranging from 5 to 500 K. The propensity rules of both collisional systems are discussed. A propensity for even Δj transitions is observed in the case of HCN–He collisions whereas a propensity for odd Δj transitions is observed in the case of HNC–He collisions. These propensities become less pronounced at high temperature, although they do not vanish within the temperature range considered in this work. The new rate coefficients will significantly help in interpreting HCN and HNC emission lines observed with current and future telescopes. In particular, the HNC/HCN abundance ratio derived from observations would have to be revised from values >1 to values ≤ 1.

Key words: molecular data – molecular processes – scattering.

1 INTRODUCTION

The estimation of molecular abundances in interstellar clouds from spectral line data at far infrared and submillimetre wavelengths may be carried out at several levels of sophistication (van der Tak et al. 2007). The choice of the method depends partly on the available collisional molecular data. Indeed, the existence of accurate collisional rates is crucial for the interpretation of molecular line observations. Without these rates, only approximate estimates of the molecular column density are possible assuming local thermodynamic equilibrium (LTE), which is generally not a good approximation (Lique et al. 2009). For molecules for which rates are known, non-LTE calculations may be performed that enable us to complete accurate column density estimates, but also estimates of kinetic temperature and volume density from spectral lines. Therefore, astrophysical models improve significantly in sophistication with the knowledge of molecular collisional rates.

Among more than 150 molecules known to exist in space, rate coefficients for collisional (de-)excitation exist for fewer than 30 and, despite recent efforts by the molecular astrophysics community, most of the rate coefficients reported have been calculated with approximate methods (Schöier et al. 2005).

An example of a key chemical species for which collisional excitation coefficients have been unavailable until now is HNC. In the absence of available collisional data for the HNC molecule, astronomers frequently used the HCN rate coefficients (Schöier et al. 2005) to estimate the abundance of HNC in molecular clouds. However, it has been shown recently by Sarrasin et al. (2010) (hereafter Paper I) that the HCN and HNC collisional rates are really different. Indeed, these authors have calculated rotational (de-)excitation rate coefficients for HCN and HNC molecules in collisions with He for temperature ranging from 5 to 100 K and found that the two sets of rate coefficients differ significantly, especially since strong propensity rules were found for even Δj in the case of HCN–He system whereas propensity rules for odd Δj were found in the case of HNC–He system.

Paper I also concluded that the HNC/HCN abundance ratio derived from observations towards dark clouds has to be revised. Indeed, the use of the HNC rate coefficients could significantly change the intensity of the HNC stimulated lines compared to those previously obtained using the HCN rate coefficients as substitutes for the HNC ones. The results of Paper I thus provided an explanation to the HNC/HCN ratio problem (Herbst, Terzieva & Talbi 2000) and

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allowed us to conclude that, in cold dark clouds, the HNC/HCN abundance ratio is $\simeq 1$.

However, as the HCN and HNC rate coefficient calculation of Paper I was limited to the 5–100 K temperature range, it seems very important to extend the work of Paper I to higher temperature in order to enable a better understanding of the HCN and HNC molecular emissions in higher temperature interstellar regions. While no high-temperature HNC collisional rate coefficients exist, rate coefficients for the rotational excitation of HCN by He atoms (employed as substitutes for H_2) at high temperature have been calculated by Green & Thaddeus (1974) and Green (unpublished).[1] However, it has been shown in Paper I that the rate coefficients of Green & Thaddeus (1974) differ from those calculated with the best available method. Hence, it also seems important to provide new HCN–He rate coefficients at high temperature.

This paper is organized as follows: Section 2 describes the potential energy surfaces (PESs) used in this work and contains a rapid description of the scattering calculations. In Section 3, we present and discuss our results.

2 METHODOLOGY OF CALCULATIONS

2.1 Potential energy surfaces

The HCN–He and HNC–He 'rigid rotor' PESs used in this work have been described in detail in Toczyłowski, Doloresco & Cybulski (2001) and in Paper I, respectively. As a reminder, they were computed *ab initio* using the single and double-excitation coupled cluster method with non-iterative triple excitations (CCSD(T)) (Hampel, Peterson & Werner 1992). The triple zeta (aug-cc-pVTZ) basis set and an additional $[3s3p2d2f1g]$ set of bond functions were used for the HCN–He van der Waals system whereas the quadruple zeta (aug-cc-pVQZ) basis set also augmented by the $[3s3p2d2f1g]$ bond functions was used for the HNC–He van der Waals system. The HCN and HNC molecules were treated as linear rigid rotors with intramolecular distances fixed at their equilibrium values ($r_{HC} = 2.013\,50$ bohr and $r_{CN} = 2.179\,23$ bohr for HCN–He; $r_{HN} = 1.8813$ bohr and $r_{NC} = 2.2103$ bohr for HNC–He]. The global minimum of the HCN–He PES is in the linear He–HCN configuration at $R = 7.97$ bohr and has a well depth of 29.90 cm^{-1}. The global minimum of the HNC–He PES was found to be –46.83 cm^{-1} ($R = 7.30$ bohr, $\theta = 180°$), corresponding to collinear He–HNC. As shown by Lique et al. (2005) and Lique et al. (2010), for such van der Waals systems where the ground electronic state is well described by a dominant configuration, the level of theory used in this work is expected to yield reliable dynamical results.

The HNC–He calculated interaction energies were fitted by means of the procedure described by Werner et al. (1989) for the CN–He system. The dependence of the PES on the He–HNC angle was fitted by the usual Legendre expansion(equation 1). From an *ab initio* grid containing 13 values of θ, we were able to include terms up to $\lambda_{\max} = 12$

$$V(R,\theta) = \sum_{\lambda} V_{\lambda}(R) P_{\lambda}(\cos\theta). \tag{1}$$

[1]The earlier calculations of Green & Thaddeus (1974) (restricted to the lowest eight levels of HCN and temperatures of 5−100 K) were extended in 1993 to obtain rate constants among the lowest 30 rotational levels and for temperatures of 100–1200 K. These unpublished results are available at http://data.giss.nasa.gov/mcrates/#hcn.

The HCN–He PES was fitted, in Paper I, using the same truncation technique as for the HC_3N–He system in Wernli et al. (2007a,b). However, the fitting method used allowed us to get a very accurate representation of the PES only for interaction energies lower than 300 cm^{-1}. For higher energies, the deviation between *ab initio* calculations and the fit was found to be large (>10 cm^{-1}). In addition, the *ab initio* calculations of Toczyłowski et al. (2001) were limited to moderate energies in the repulsive wall. As, in this work, we were mainly interested in the determination of rate coefficients at high temperature, we have decided to perform new HCN–He *ab initio* calculations in order to obtain a new analytical fit of the HCN–He PES using the same procedure than the one used for HNC–He. Hence, we have obtained new *ab initio* values for the repulsive wall using the same methodology than the one described in detail in Toczyłowski et al. (2001) and the HCN–He PES was fitted by the usual Legendre expansion (equation 1). From an *ab initio* grid containing 11 values of θ, we were able to include terms up to $\lambda_{\max} = 10$. The largest deviations between the fit and the *ab initio* points occur primarily in the repulsive region of the PES. Over the entire grid, the mean relative difference between the analytic fit and the *ab initio* calculations is 2 per cent.

We recall that, for the HCN–He system, the largest (in magnitude) of the anisotropic terms ($\lambda > 0$) corresponds to $\lambda = 2$. This implies that, to a first approximation, the PES is symmetric with respect to $\theta \rightarrow \pi - \theta$. At the opposite, for the HNC–He system, the largest of the anisotropic terms corresponds to $\lambda = 1,\ 3$ in the relevant range of R, i.e. between 7 and 8 bohr. This reflects a large (odd) anisotropy for the PES. Consequences for the rotational excitation will be discussed in the next section.

2.2 Dynamical calculations

The main focus of this paper is the use of the two fitted HCN–He and HNC–He PES to determine rotational excitation and de-excitation cross-sections of HCN and HNC molecules by He atoms. In the following, the rotational quantum number of HCN and HNC will be denoted j. Despite the presence of a hyperfine structure in both molecules (Garvey & de Lucia 1974), we consider here only the rotational structure of HCN and HNC.

To determine the inelastic cross-sections, we used the exact close-coupling (CC) approach of Arthurs & Dalgarno (1960). The integral cross-sections are obtained by summing the partial cross-sections over a sufficiently large number of values of the total angular momentum J until convergence is reached.

The standard time-independent coupled scattering equations were solved using the MOLSCAT code (Hutson & Green 1994). Calculations were carried out at values of the total energy ranging from 3.2 to 3500 cm^{-1}. The integration parameters were chosen to ensure convergence of the cross-sections. We extended the rotational basis sufficiently to ensure convergence of the inelastic cross-sections for $j, j' \leq 25$. At the largest total energy considered (3500 cm^{-1}), the HCN and HNC rotational basis extended to $j = 35$ and 34, respectively. The maximum value of the total angular momentum J used in the calculations was set large enough that the inelastic cross-sections were converged to within 0.005 Å^2.

From the rotationally inelastic cross-sections $\sigma_{j\rightarrow j'}(E_c)$, one can obtain the corresponding thermal rate coefficients at temperature T_K by an average over the collision energy (E_c):

$$k_{j\rightarrow j'}(T_K) = \left(\frac{8}{\pi\mu k_B^3 T_K^3}\right)^{\frac{1}{2}} \times \int_0^{\infty} \sigma_{j\rightarrow j'}(E_c)\, E_c\, e^{\frac{-E_c}{k_B T_K}}\, dE_c, \tag{2}$$

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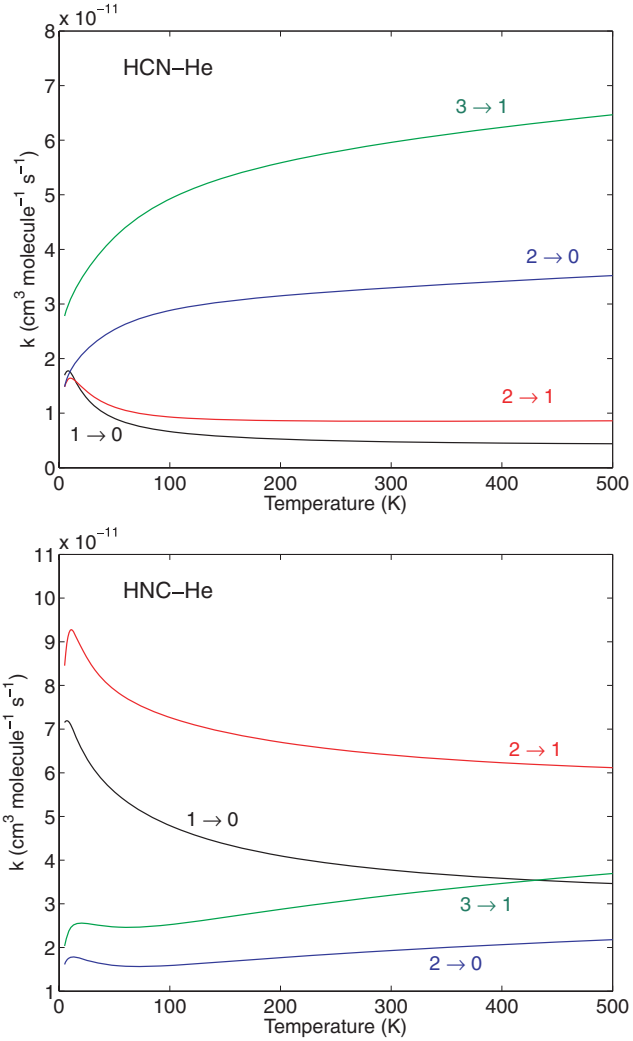

Figure 1. Typical rate coefficients for the HCN (upper panel) and HNC (lower panel) molecules in collision with He as a function of the temperature.

where μ is the reduced mass and k_B is Boltzmann's constant. To obtain precise values for the rate coefficients, the energy grid was chosen to be sufficiently fine to include the numerous scattering resonances. Calculations up to 3500 cm^{-1} allow us to determine rates up to 500 K.

3 RESULTS

3.1 Rate coefficients

We have calculated the energy dependence of the collisional (de-)excitation cross-sections using the computational scheme described above for transitions between the first 26 ($j = 0$–25) rotational levels of HCN and HNC. Then, we have obtained, by energy averaging, de-excitation rate coefficients for the first 26 rotational levels of HCN and HNC, from the CC cross-sections. The representative variation with temperature is illustrated in Fig. 1.

This complete set of (de-)excitation rate coefficients is available online from the LAMDA[2] and BASECOL[3] websites. Excitation rate coefficients can be easily obtained by detailed balance:

$$k_{j\to j'}(T_K) = k_{j'\to j}(T_K)\frac{2j'+1}{2j+1}\exp[-(\varepsilon_{j'}-\varepsilon_j)/k_B T_K], \quad (3)$$

where ε_j and $\varepsilon_{j'}$ are, respectively, the energies of the rotational levels j and j'.

As mentioned in the introduction, HCN–He rate coefficients were already provided by Green & Thaddeus (1974) and Green (unpublished). Table 1 compares on a small sample the temperature dependence of our HCN–He rates versus those of Green & Thaddeus (1974) and Green (unpublished).

One can see a global agreement between the two sets of rate coefficients. However, we found some difference that can be up to a factor of 2 and has important consequence on astrophysical modelling. These differences can be attributed to the use of a new PES for the scattering calculations. The differences decrease with increasing temperature (see e.g. the 3 → 0 transition).

3.2 Comparison between HCN and HNC rate coefficients

In the absence of available collisional data for the HNC molecule, rate coefficients of HCN are frequently used (Schöier et al. 2005) to estimate the column density of HNC in molecular clouds. In order to check the validity of this approach, we have decided to compare both sets of rate coefficients.

Fig. 2 shows the HCN–He and HNC–He de-excitation rate coefficients from the $j = 10$ level at 100 and 500 K. One can see that significant differences exist between the HCN–He and HNC–He rate coefficients (see also Table 1). The propensity rules seen in the two sets of rate coefficients are different. The HCN–He rate coefficients present a strong propensity in favour of transitions with even Δj whereas the HNC–He rate coefficients present a strong propensity in favour of transitions with odd Δj. These propensities were already found and explained in Paper I for low-temperature rate coefficients.

However, one can see that the importance of the propensity in favour of transitions with odd Δj for HNC–He rate coefficients decreases with increasing temperature. Indeed, the intensities of $\Delta j = 2$ transitions double when the temperature goes from 100 to 500 K whereas the intensities of the $\Delta j = 1$ transitions is almost constant with increasing temperature. This behaviour can be explained by looking at the energy variations of the cross-sections. Fig. 3 illustrates the typical energy dependence of the HNC–He and HCN–He de-excitation cross-sections from the $j = 10$ levels.

One can see that for HNC–He the $j = 10 \to 9$ cross-section matches the $j = 10 \to 8$ one at high collisional energy, whereas for HCN–He the cross-sections never cross. This crossing explains the trend seen above. The origin of this behaviour comes from the evolution of the anisotropy from the long- to the short-range regimes. For the HNC–He system, the largest of the anisotropic terms of the angular expansion (equation 1) corresponds to $\lambda = 1, 3$ between 7 and 8 bohr and to $\lambda = 2$ for shorter R distance (see fig. 2 in Paper I). As short-range interactions mainly affect the collisions at high energies, it explains that the magnitude of HNC rates for even Δj transitions increases at high collisional energies.

From this comparison, one can see that the use of HCN rate coefficients, in astrophysical applications, in order to interpret HNC observations may be dangerous, even at high temperatures, since the use of 'real HNC rate coefficients' will probably significantly modify the excitation of the HNC molecule. In Paper I, one has shown that the HNC/HCN abundance ratio derived from observations has to be revised down in the 5–100 K temperature range. One

[2]http://www.strw.leidenuniv.nl/~moldata/
[3]http://basecol.obspm.fr/

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Table 1. HCN–He and HNC–He rate coefficients at 100, 200 and 400 K in 10^{-10} cm^3 molecule^{-1} s^{-1}.

	100 K			200 K			400 K		
$j \rightarrow j'$	HCN	GT74	HNC	HCN	GT74	HNC	HCN	GT74	HNC
$1 \rightarrow 0$	0.063	0.054	0.479	0.052	0.049	0.410	0.045	0.044	0.358
$2 \rightarrow 0$	0.288	0.286	0.159	0.315	0.298	0.177	0.342	0.306	0.207
$2 \rightarrow 1$	0.093	0.095	0.727	0.086	0.094	0.670	0.085	0.091	0.623
$3 \rightarrow 0$	0.010	0.021	0.093	0.014	0.022	0.105	0.018	0.022	0.111
$3 \rightarrow 1$	0.492	0.460	0.252	0.559	0.507	0.287	0.624	0.550	0.347
$3 \rightarrow 2$	0.091	0.114	0.783	0.099	0.118	0.758	0.108	0.118	0.736
$5 \rightarrow 0$	0.006	0.012	0.037	0.010	0.014	0.051	0.013	0.015	0.061

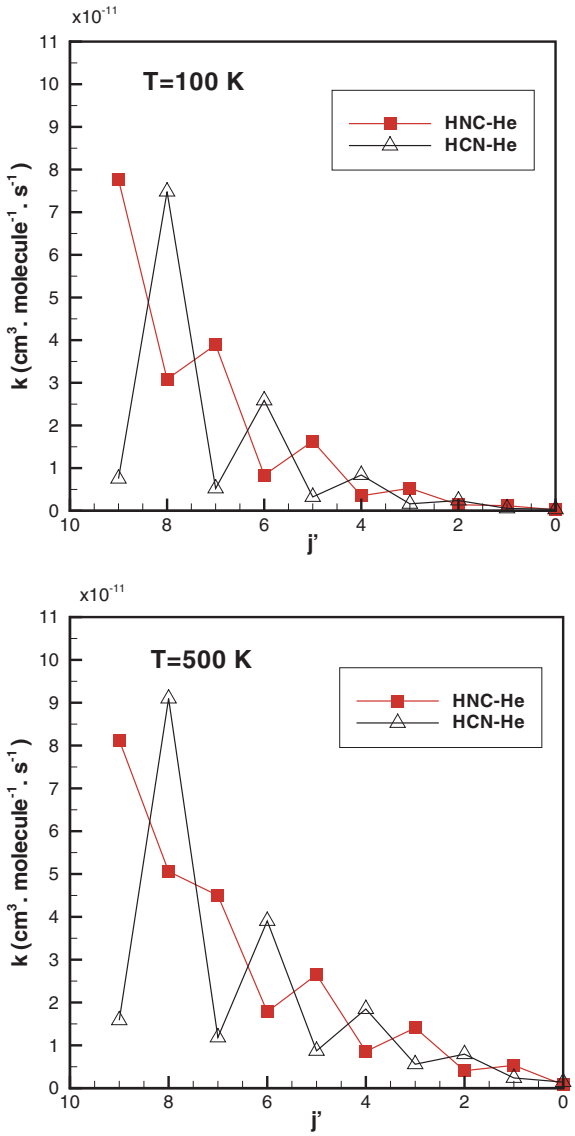

Figure 2. HCN–He and HNC–He de-excitation rate coefficients from the initial level $j = 10$ at 100 K (upper panel) and 500 K (lower panel).

could anticipate that the use of the present rate coefficients will also decrease the ratio derived from molecular clouds emission at higher temperature. However, the decrease should be reduced at temperature closed to 500 K. On the other hand, it is quite hard to anticipate the astrophysical consequence of the use of the new rate coefficients since the radiative transfer does not vary linearly with the rate coefficients and one has to perform specific calculations with the new rate coefficients to accurately evaluate the consequences.

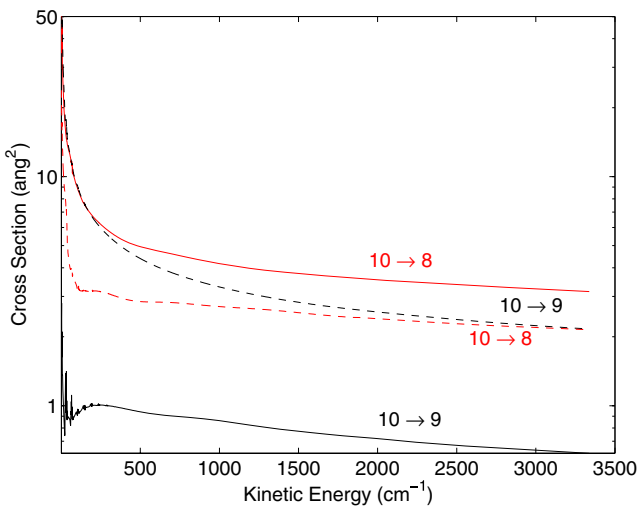

Figure 3. HNC–He (full line) and HCN–He (dashed line) de-excitation cross-sections from the $j = 10$ levels as a function of the collision energy.

We note, finally, that the temperature dependence of the rates, as illustrated in Fig. 1, is different for different transitions, suggesting that extrapolation in temperature above 500 K is hazardous. Dedicated scattering calculations, possibly including the bending mode of HCN (which lies at 713 cm^{-1} above the ground vibrational level), will be therefore necessary to go higher in temperature.

4 SUMMARY AND CONCLUSION

We have used quantum scattering calculations to investigate rotational energy transfer in collisions of HCN and HNC molecules with He atoms. The calculations are based on recent, highly accurate two-dimensional PESs. Rate coefficients for transitions involving the lowest 26 levels of these molecules were determined for temperatures ranging from 5 to 500 K. Strong propensity rules for even Δj were found in the case of HCN–He system whereas propensity rules for odd Δj were found in the case of HNC–He system.

These results also indicate that the HNC/HCN abundance ratio derived from observations towards molecular clouds has to be revised. Indeed, the use of the HNC rate coefficients will significantly change the intensity of the HNC stimulated lines compared to those previously obtained using the HCN rate coefficients as substitutes for the HNC ones.

Finally, the great abundance of H_2 in the interstellar medium makes this molecule the primary collision partner for any other

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species. It is generally assumed (Lique et al. 2008) that rate coefficients with He can provide a good estimate of rate coefficients for collision with para-$H_2(j = 0)$. Recent results on rotational excitation of CO (Wernli et al. 2006), SO (Lique et al. 2007) and SiS (Lique & Kłos 2008; Kłos & Lique 2008) have pointed out that rate coefficients for collisions with para-$H_2(j = 0)$ can be up to a factor of 3 larger or smaller than those for collisions with He, depending on the selected transition, but that the He rate coefficients scaled by a factor of 1.4 provide the correct order of magnitude of the $H_2(j = 0)$ rate coefficients. Therefore, the present results should provide a reasonable first estimate of collisional rate coefficients for collisions of HCN and HNC with para-$H_2(j = 0)$. On the other hand, it may be unadvisable to use the present He rate coefficients as an estimate of the ortho-H_2 rate coefficients, since the He and ortho-H_2 rate coefficients usually differ significantly. Specific calculations with ortho-H_2 must be performed. Thus, it is crucial to extend the calculations, both of the PES and of the inelastic cross-sections, to the HCN–H_2 and HNC–H_2 systems.

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