THE ROTATIONAL EXCITATION OF AlCN AND AlNC BY He

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Introduction

Cyanide/isocyanide species are the most common metal-containing molecules in circumstellar gas[1,2]. These compounds have been detected since the 90's in different interestellar sources like IRC+10216 and CRL2688 stars. Among the cyanide and isocyanide molecules, AlNC, along with MgCN and MgNC, are of particular interest since heavy metals in the gas phase are important in controlling the ionization of a cold dark cloud and hence the chemistry and finally the cloud evolution. AlNC was first observed in the IRC+10216 circumstellar shell. In contrast, the other two Al-bearing molecules previously detected, AlF and AlCl, AlNC exist exclusively near the stellar photosphere and then can be used as a tracer of these region. To the best of our knowledge the other isomer of AlNC, the AlCN molecule has not been yet been detected in space despite the molecule is suspected to be there[3]. The estimation of molecular abundances in interestellar clouds from spectral line data could be carried out with a high level of sofistication if accurate collisional rates data are available. In this work we present new rotational rate coefficients for AlNC and AlCN based on highly accurate, AlCN–He and AlNC–He potential energy surface (PES)[4]. This poster is organized in two main parts. Section "Theory of rotational excitation process" present a brief description of methodology used to obtain the PES and to perform the dynamical calculations. Section "Dynamical calculations" show results, and discuss them.

Theoty of rotational exitation process

Potentia energy surfaces (PES). The AlCN and AlNC rigid rotor PES were computed *ab initio* using the CCSD(T) method[5], with a triple zeta (aug-cc-pVTZ) basis set and an additional [3s3p2d2f 1g] set of bond functions.

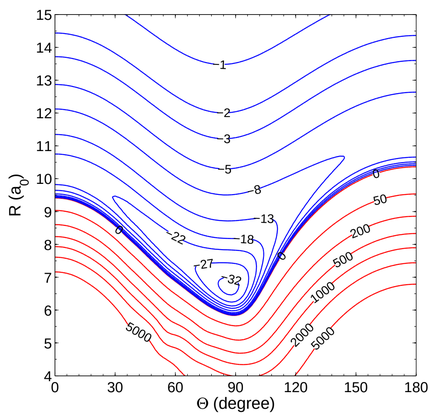

Figure 1: Contour plot of the He-AlCN PES

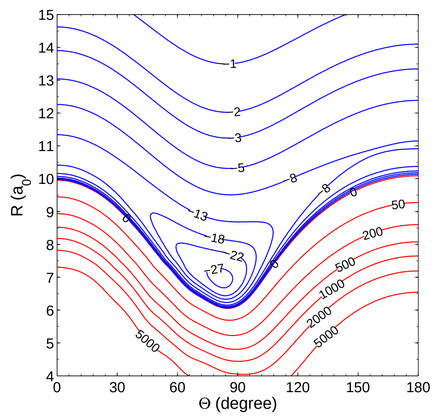

Figure 2: Contour plot of the He-AlNC PES

The AlCN and AlNC molecules were treated as linear rigid rotors with intramolecular distances fixed at their equilibrium values [r_{AlC} =3.83 bohr and r_{CN} =2.21 bohr for AlCN–He ; r_{AlN} = 3.54 bohr and r_{NC} = 2.243 bohr for AlNC–He]. As shown by Lique et al. in previous works[6,7], 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 scattering of an atom by a rigid rotator. The collisional proscess is study solving the time–independent Shrodinger equation. The Hamiltonian of the system may be written

$$\left[\frac{\mathbf{j^2}}{2I} + \frac{\nabla_R^2}{2\mu} + V(R,\theta')\right]\Psi = E\Psi$$

where $\mathbf{j}^2/2I$ is the target Hamiltonian and $V(R,\theta')$ and $\nabla_R^2/2\mu$ describe the potential energy interaction and kinetic energy of the atom-molecule system in the centre of mass frame respectively. Because the full Close Coupling (CC) approach is very computationally intensive for molecules with small rotational constants, we used the Coupled-States approximation for the determination of cross sections. The standard time-independent coupled scattering equations were solved using the MOLSCAT code[8]. Calculations were carried out at values of the total energy up to 1000 cm^1 . The integration parameters were chosen to ensure convergence of the cross sections over this range and for $j, j' \leq 25$.

The CS approach is expected to give accurate results at high energies and for transitions between high rotational levels for a heavy system like AlCN/AlNC. However, errors can arise whenever weak collisions at large impact parameter make a significant contribution, as will occur at low energies or for transitions between closely-spaced levels.

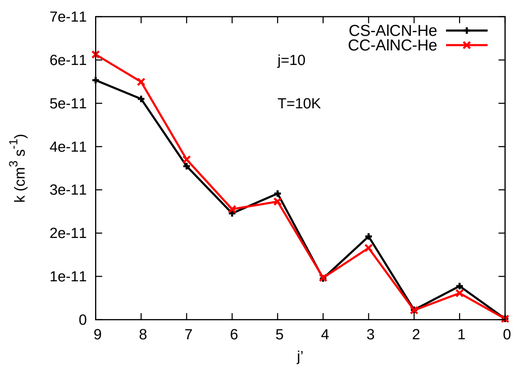

Figure 3: Compares AlNC-He CC and CS rate coefficients at 10K.

One can see that CC and CS results are in good agreement, even at 10K and we have decided to use the CS approximation to determine the inelastic rate coefficients.

Dynamical calculations.

Rotational cross-sections. 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.

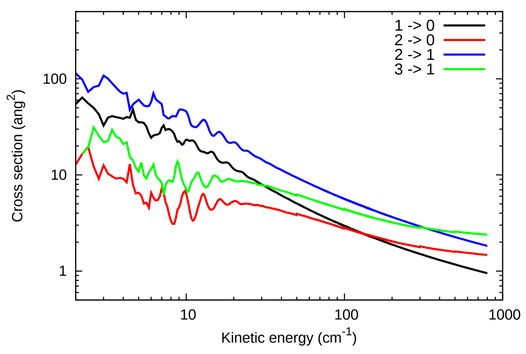

Figure 4: Rotational de-excitation cross–sections for AlCN

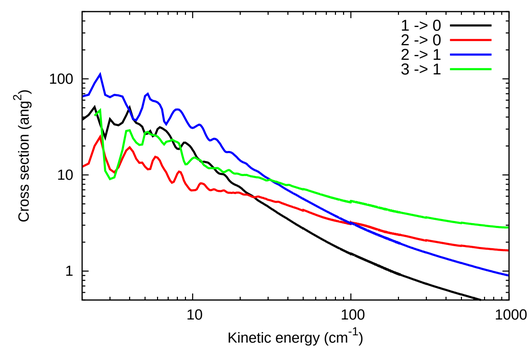

Figure 5: Rotational de-excitation cross–sections for AlNC

Thermal rate coefficients. From the rotational inelastic cross-sections $\sigma_{j\to j'}(Ec)$, one can obtain the corresponding thermal rate coefficients at temperature T_K by an average over the collision energies (Ec).

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

where μ is the reduced mass and k_B is the Boltzmann's constant.

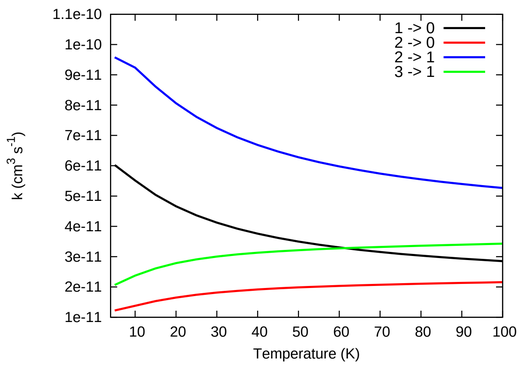

Figure 6: Rate coefficients for the AlCN–He collisional systems

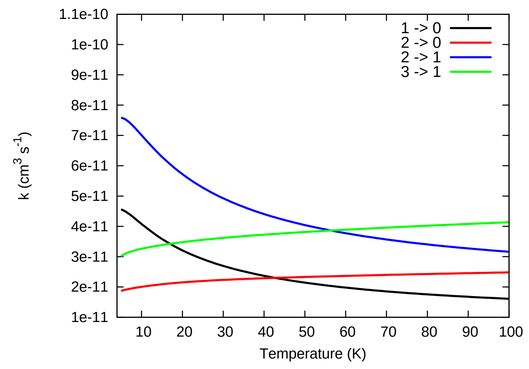

Figure 7: Rate coefficients for the AlCN–He collisional systems

Comparisons between AlNC and AlCN.

1. At low temperetures significant differences exist between the AlNC–He and AlCN–He rates. In this case the AlCN–He collisional systems present an stronger propensity in favour of transitions with odd Δj than the AlCN–He systems.
2. At higher temperatures both systems presents the same markable odd propensity rules which are related with the asymmetry of the two PES.

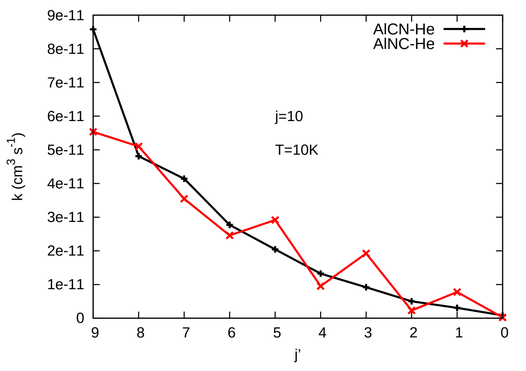

Figure 8: AlNC–He and AlCN–He de–excitation rate coefficients at 10 K

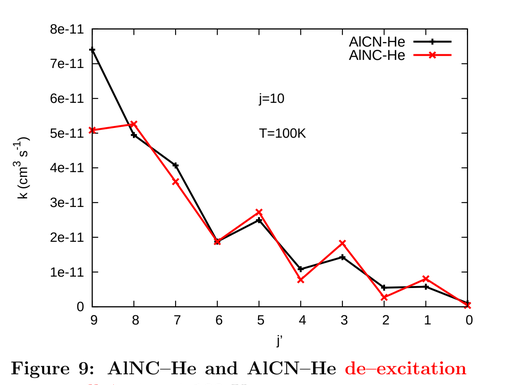

Figure 9: AlNC–He and AlCN–He de–excitation rate coefficients at 100 K

Conclusion

We have used quantum scattering calculations to investigate rotational energy transfer in collisions of AlNC and AlCN molecules with He atoms. The rates $k_{1\to 0}$ at different temperatures suggest that more intense $\Delta j = 1$ spectral line should be expected for AlCN-He collisional system. However if it is considered that the AlNC isomer is more stable and that is the only one detected in the interestellar space we can predict the AlCN/AlNC ratio to be <<1. The new rate coefficients obtained in this work should help to discover the AlCN molecule in molecular clouds and also could be useful for later estimations of AlCN/AlNC abundances ratio in cold clouds in the Interstellar Medium.

References

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