



# Anions chemistry in the interstellar medium

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## Abstract

During the last decade, several anions have been detected in the interstellar and circumstellar media. The detections of anions have led to interesting research on chemistry of negative molecular ions. We present some examples of the contribution of physical chemistry to the ISM anions chemistry research. Modeling of anion emission spectra requires the calculation of rates for rotational excitation by collisions with H<sub>2</sub>. We report the first collisional data for an interstellar anion, the rate coefficients for the rotational excitation of CN<sup>-</sup> by H<sub>2</sub>. State-to-state rate coefficients were calculated for temperatures ranging from 5 to 100 K. The CN<sup>-</sup> rate coefficients are compared with those of the neutral CO molecule and, as expected, it is found that the rate coefficients for the anion are significantly larger than the ones of the neutral species. We also show how first principles calculations can predict the existence of new molecular anions. We predict the existence of the N<sub>2</sub>H<sup>-</sup> anion. We present the global potential energy surface and the bound states of the N<sub>2</sub>H<sup>-</sup> van der Waals anion. The electronic calculations were performed using state-of-the-art *ab initio* methods and the nuclear motions were solved using a quantum close-coupling scattering theory. We also present the absorption spectra of the N<sub>2</sub>H<sup>-</sup> complex.

## Rotational excitation of CN<sup>-</sup> by H<sub>2</sub>

The potential energy surface [1] was calculated within the supermolecular approach using a CCSD(T) method. In all calculations, to determine the interaction potential  $V(r, R, \theta, \theta', \phi)$ , the basis set superposition error (BSSE) was corrected at all geometries. The four atoms were described by the aug-cc-pVTZ augmented by the (3s, 2p, 1d) bond functions, placed at mid-distance between the CN<sup>-</sup> and H<sub>2</sub> centers of mass.

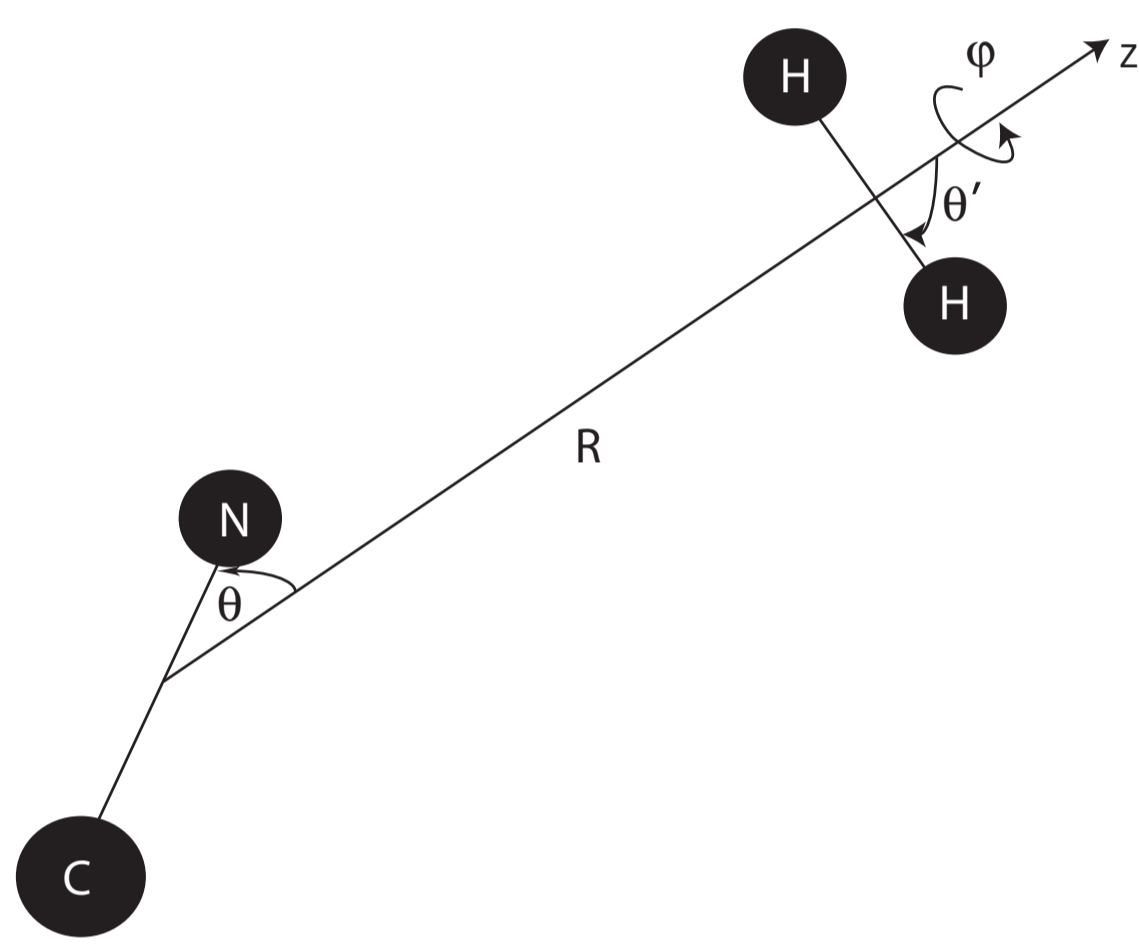


Fig. 1 : Body-fixed Jacobi coordinates of CN<sup>-</sup>-H<sub>2</sub>

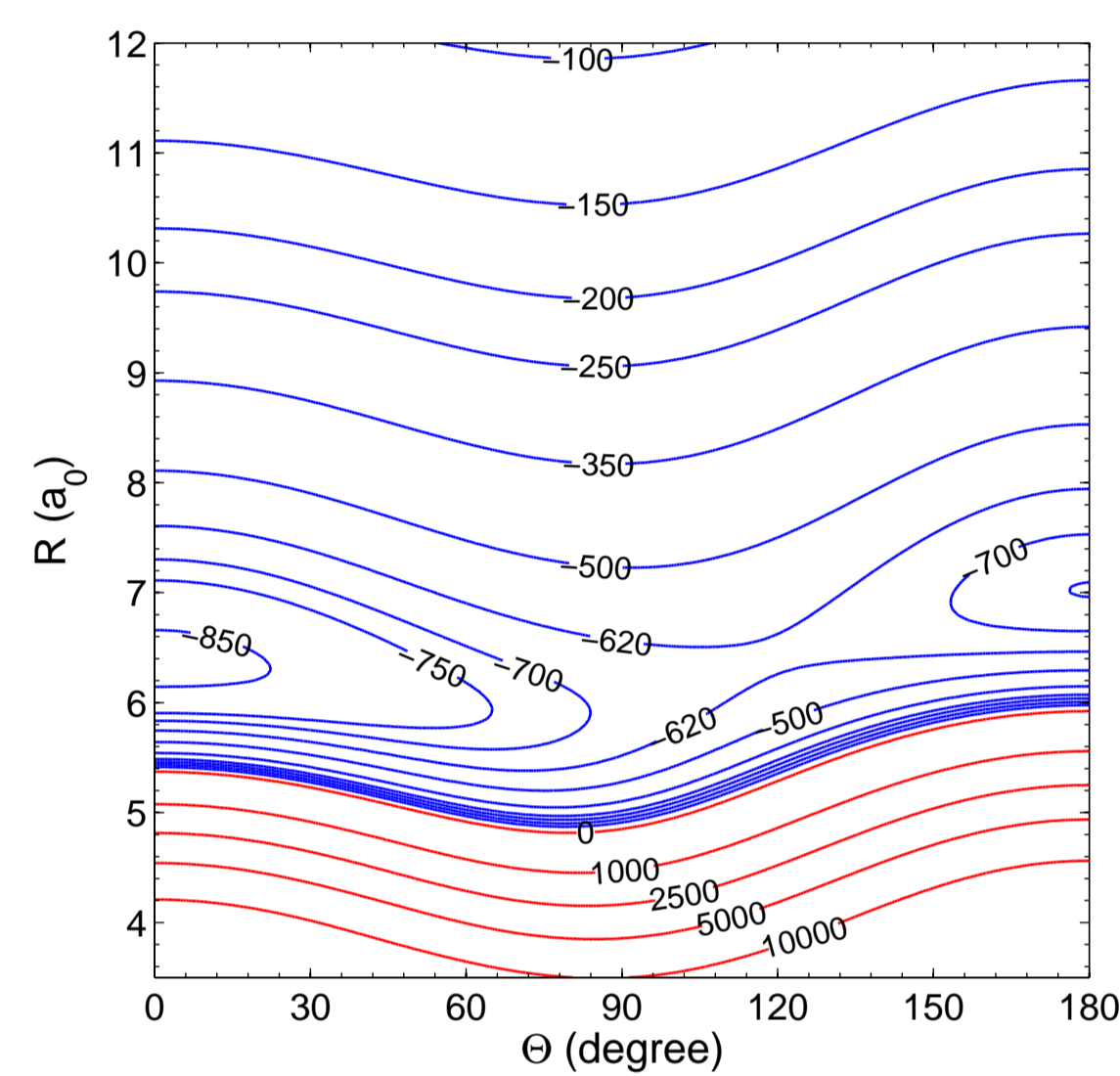


Fig. 2 : Contour plot of the CN<sup>-</sup>-H<sub>2</sub> PES for the H<sub>2</sub> orientation corresponding to the minimum energy.

The global minimum of the  $V_{v=0}(R, \theta, \theta', \phi)$  PES is located at  $R = 6.38 a_0$  for the collinear C-N...H-H geometry ( $\theta = 0, \theta' = 0$ ) with a well depth of 875.4 cm<sup>-1</sup>. The depth of this well comes from the charge interaction with quadrupole and higher moments of the H<sub>2</sub> molecule and other induction or dispersion terms. Figure 2 represents the cut of the PES for  $\theta' = 0^\circ$  and  $\phi = 0^\circ$ .

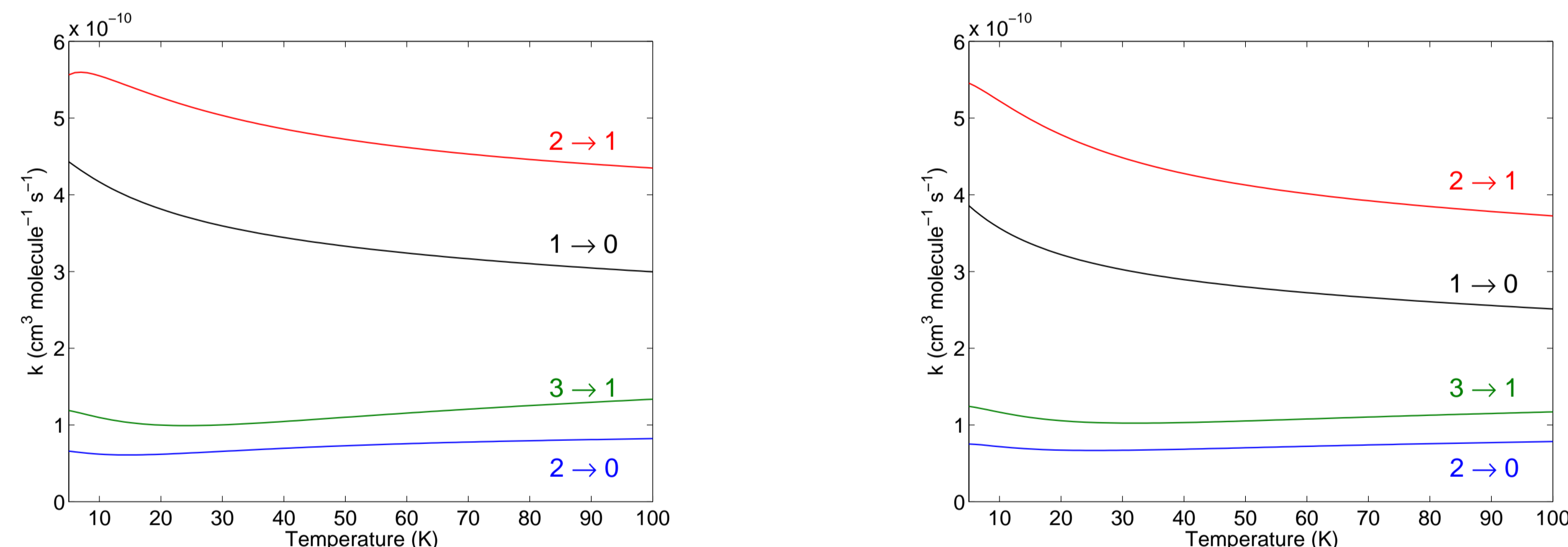


Fig. 3 : Temperature variation of collisional de-excitation rate coefficients of CN<sup>-</sup> by : Panel a) para-H<sub>2</sub>( $j_2 = 0$ ) and Panel b) ortho-H<sub>2</sub>( $j_2 = 1$ )

Figure 3 illustrates the variation with temperature of the de-excitation rate coefficients of CN<sup>-</sup> in collision with para-H<sub>2</sub>( $j_2 = 0$ ) and ortho-H<sub>2</sub>( $j_2 = 1$ ). One can see that there are no significant differences between the collisions with the two species of H<sub>2</sub>. It is interesting to note that for collisions with both para- and ortho-H<sub>2</sub>, inelastic rate coefficients with  $\Delta j_1 = 1$  are larger than those with  $\Delta j_1 = 2$ .

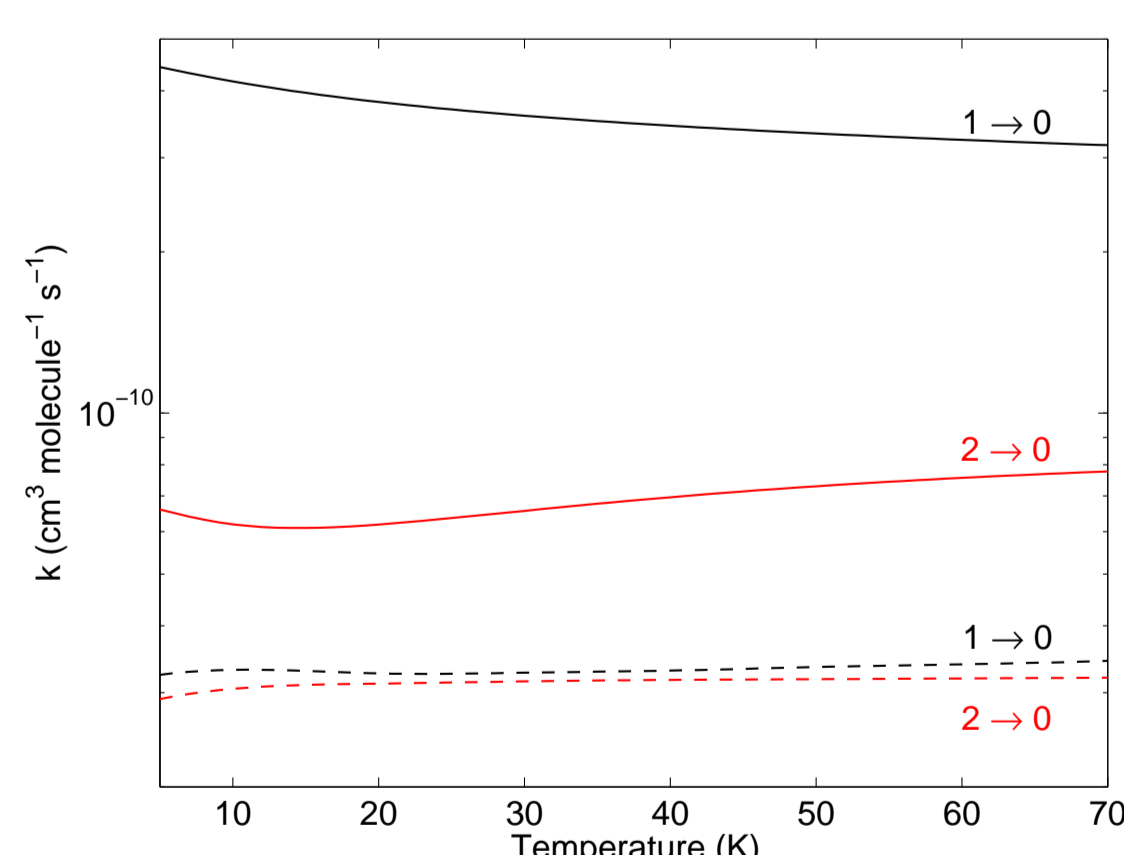


Fig. 4 : Temperature variation of the CN<sup>-</sup> (solid lines) and CO (dashed lines) de-excitation rate coefficients for collisions with para-H<sub>2</sub>( $j_2 = 0$ )

The large difference can be explained by the shape of the PES. The well depth of the CO-H<sub>2</sub> PES is 93 cm<sup>-1</sup> whereas the one of CN<sup>-</sup>-H<sub>2</sub> PES is 875 cm<sup>-1</sup> which is about 9 times larger. This comparison shows that the impact of collision will be more important for interstellar anions than for neutral species but also that neutral rate coefficients cannot be used for modeling of interstellar line emissions of anions.

The CO molecule is isoelectronic with CN<sup>-</sup> and has the same ground electronic state <sup>1</sup>Σ<sup>+</sup>. Hence, we compare in Fig. 4, on a small data sample, the temperature variation of the de-excitation rate coefficients of CN<sup>-</sup> in collisions with H<sub>2</sub>( $j_2 = 0$ ) with those obtained recently for the neutral CO molecule in collision with H<sub>2</sub>( $j_2 = 0$ ). On can clearly see that the CN<sup>-</sup> rate coefficients are significantly larger than those of CO. Indeed, the CN<sup>-</sup>-H<sub>2</sub>( $j_2 = 0$ ) rate coefficients are up to a factor of ten larger than the one of CO-H<sub>2</sub>( $j_2 = 0$ ).

## N<sub>2</sub>H<sup>-</sup> : a new interstellar anion ?

The N<sub>2</sub>H<sup>-</sup> anionic complex was first characterized by calculations at the CCSD(T) level. Some complementary calculations have also been done with the CASSCF method, followed by the MRCI approach. A large diffuse basis set of aug-cc-pV5Z quality is used for the description of the nitrogen and hydrogen atoms. The present work uses a Jacobi coordinate system, in which  $r$  is the N<sub>2</sub> internuclear distance,  $R$  is the distance from the center of mass of N<sub>2</sub> to the H<sup>-</sup> atom and  $\theta$  is the angle between the two distance vectors.

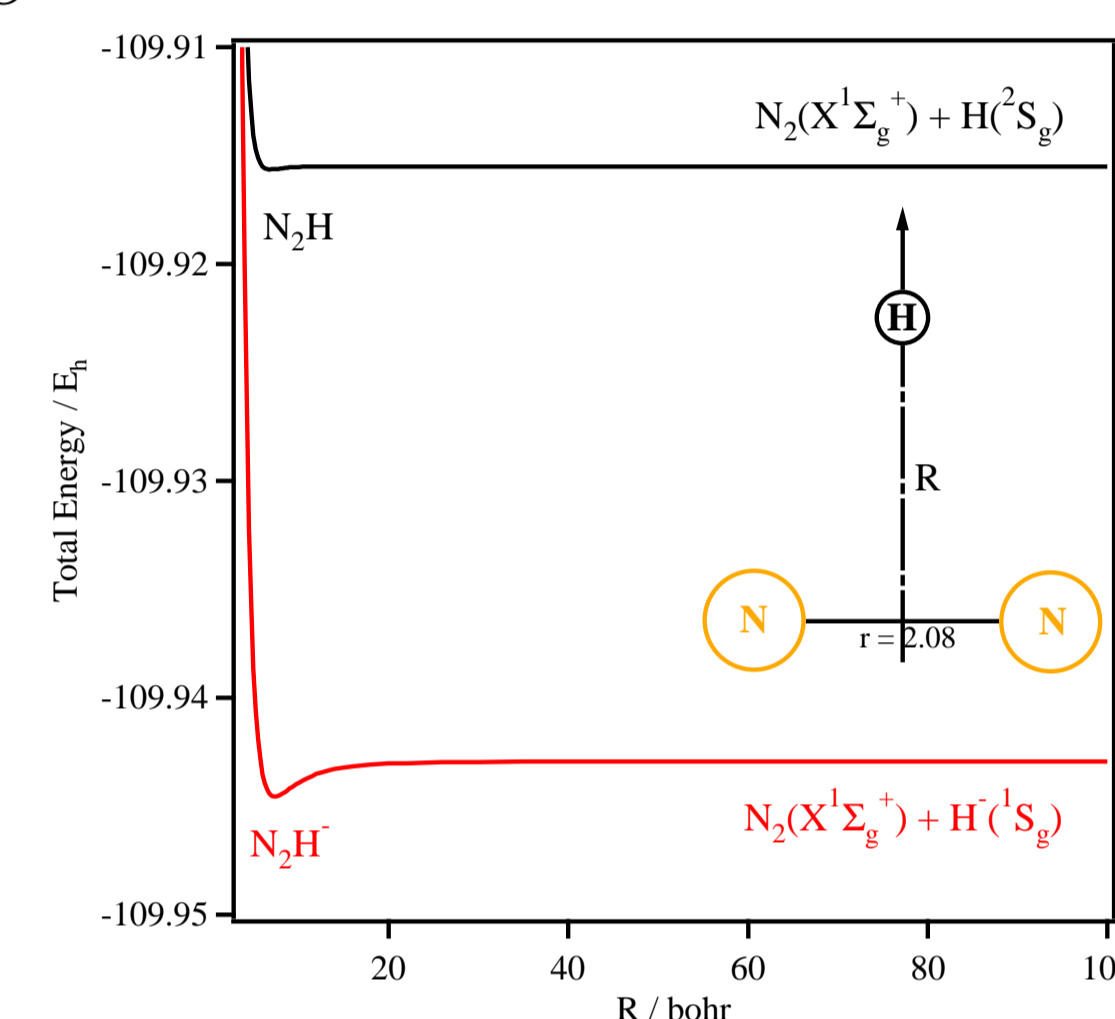


Fig. 5 : (R)CCSD(T)/aug-cc-pV5Z cuts of the ground 3D PESs of N<sub>2</sub>H and N<sub>2</sub>H<sup>-</sup> vs. the  $R$  Jacobi coordinate.  $r = 2.08$  bohr and  $\theta = 90^\circ$ . The energies are in E<sub>h</sub>.

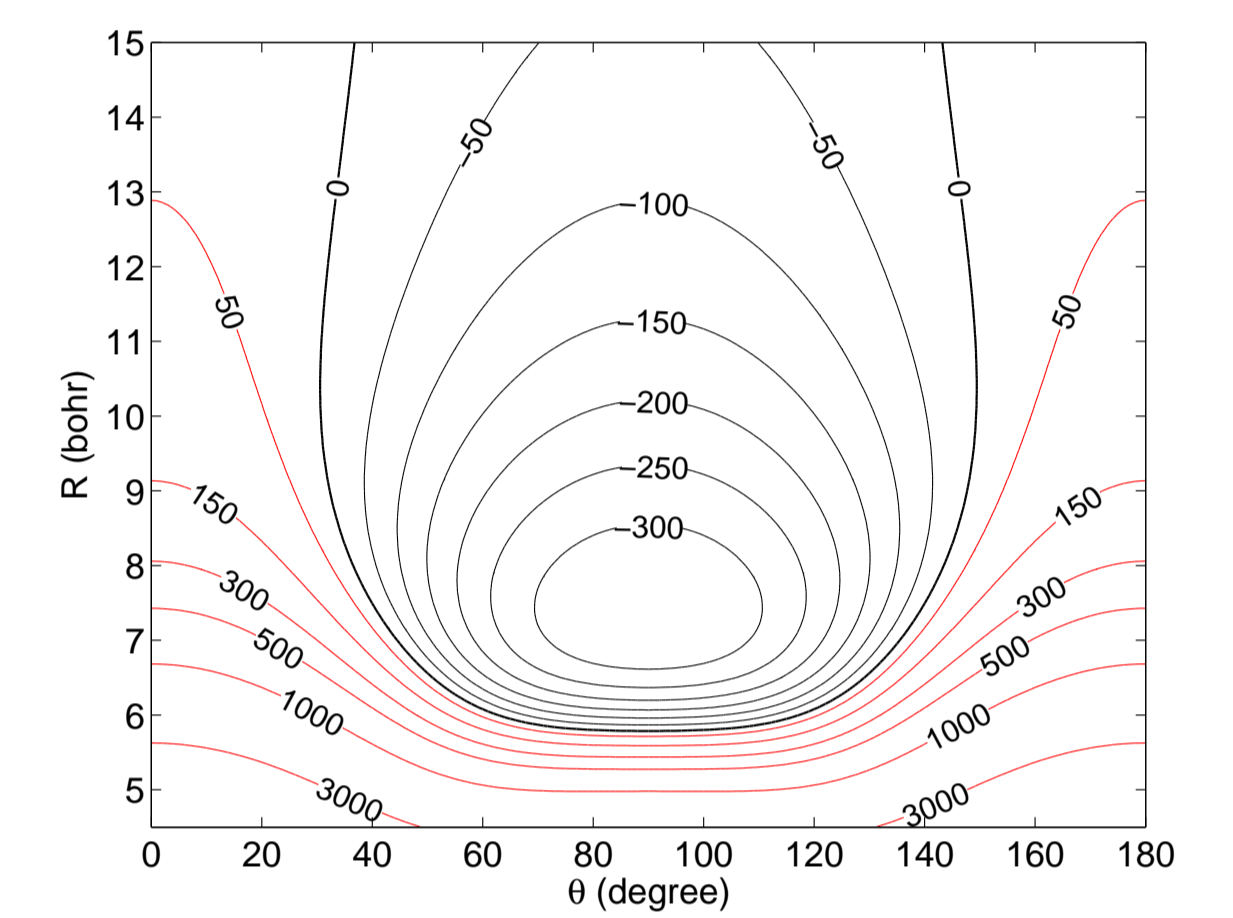


Fig. 6 : Contour plot (in cm<sup>-1</sup>) of PES of the N<sub>2</sub>H<sup>-</sup> system as a function of Jacobi coordinates  $R$  and  $\theta$ . The N<sub>2</sub> bond length is held fixed to 2.08 bohr.

Our calculations reveal that the N<sub>2</sub>H<sup>-</sup> anion is stable. Indeed, Figure 5 shows that the PES of N<sub>2</sub>H<sup>-</sup> is lying below the PES of the neutral N<sub>2</sub>H electronic ground state and that this potential is located solely so that it is free from any interaction with any neighbouring electronic state that may participate into its depletion. Then, the complex PES was calculated at CCSD(T)/aug-cc-pV5Z level of theory [2]. Figure 6 depicts the 2D contour plot of our 3D PES as a function of  $R$  and  $\theta$  for  $r = r_e = 2.08$  bohr. Obviously, the PES presents strong anisotropies with respect to the H<sup>-</sup> rotation around N<sub>2</sub>. The long range interaction energy is particularly intense and retain significant value even at notably large separation of the monomers. This results from the charge-quadrupole and the charge-induced dipole interactions which vary as  $R^{-3}$  and  $R^{-4}$ , respectively.

We also determined the N<sub>2</sub>H<sup>-</sup> vibrotational spectra, which is a prerequisite before an interstellar search for the anion can be performed by radioastronomy or by far-IR detection. The energies of the bound states have been calculated with the close-coupling scattering method [3]. Figure 7 presents the microwave and the far infrared spectra of the N<sub>2</sub>H<sup>-</sup> complex within the 0 - 100 cm<sup>-1</sup> frequency range.

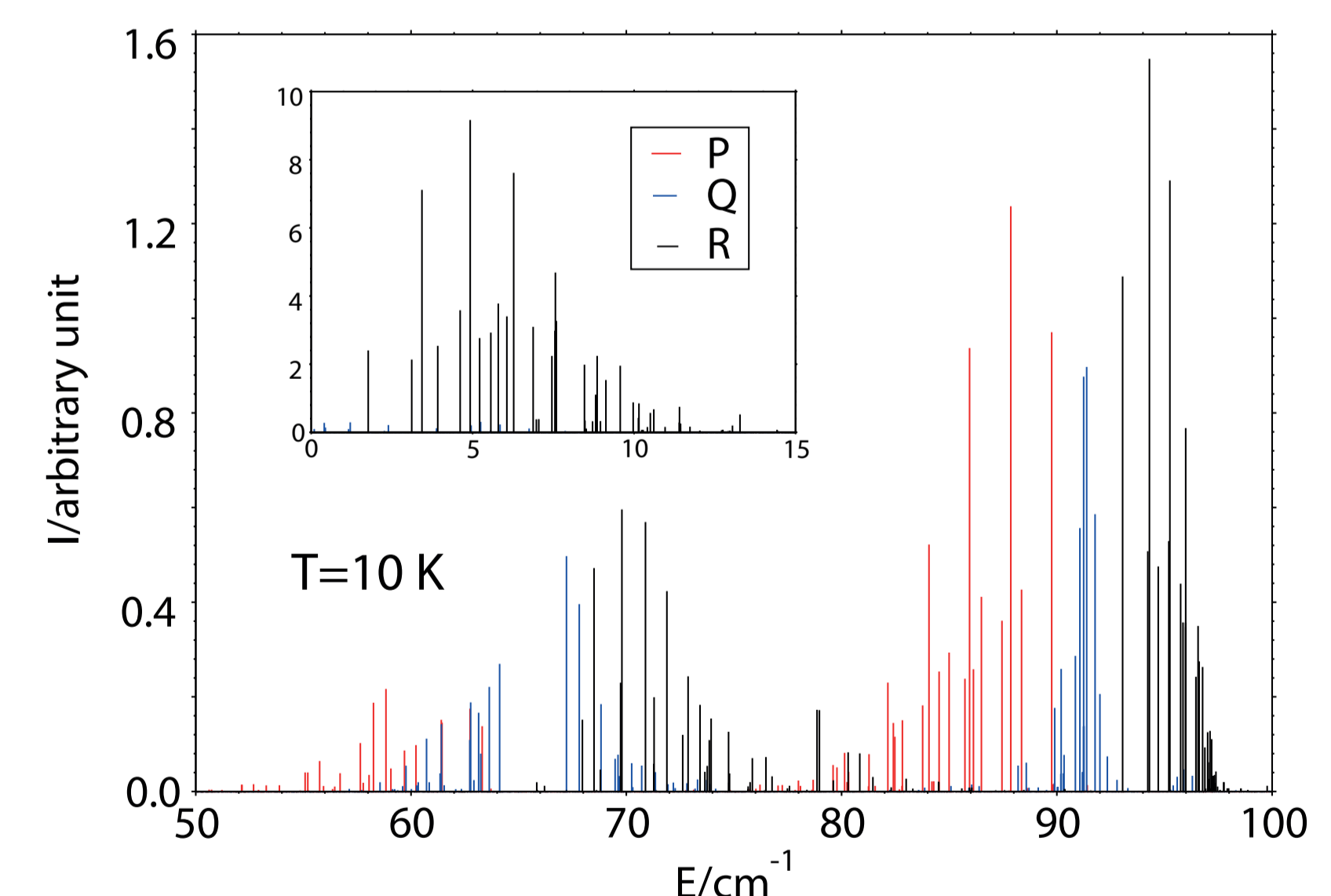


Fig. 7 : Microwave and far-infrared spectra of the N<sub>2</sub>H<sup>-</sup> complex.

This anion is an asymmetric type rotor with  $A_e = 59564$  MHz,  $B_e = 34150$  MHz and  $C_e = 21706$  MHz. The asymmetry parameter  $\kappa$  is equal -0.34, which makes this anion neither a close prolate nor close oblate symmetric rotor. The microwave spectrum (close to zero frequencies) consists of a dominant R branch and less intense Q branch and a very low intensity P branch (four orders of magnitude lower than the R branch). The low intensity of the P branch is related to the low temperature used for generating this spectrum ( $T = 10$  K). Then the spectrum is composed by a gap followed by two bands centred at  $\sim 66$  and  $\sim 91$  cm<sup>-1</sup>. These bands extend over 20 - 30 cm<sup>-1</sup>. Both of them exhibit a PQR structure. These branches are of almost the same order of magnitude within a specific band. These bands correspond to the population of the rovibrational levels ( $\nu_b = 1, \nu_s = 0$ ) and ( $\nu_b = 0, \nu_s = 1$ ) respectively. The intensities of the first band (bending) are four-five times lower than the second one (stretching) for which more favorable selection rules are expected for intermonomer stretching mode. Our spectra represent predictions.

## Conclusion

The CN<sup>-</sup>-H<sub>2</sub> rate coefficients are the first one for this molecule, but also for an interstellar anions. Taking into account the importance of the anions in the interstellar chemistry, we expect that these results will help in the interpretation of the CN<sup>-</sup> emission lines observed with current and future telescopes [4]. The N<sub>2</sub>H<sup>-</sup> complex could be used as a tracer of the H<sup>-</sup> ion in ISM, which presence was suggested but never established. More interestingly, the stable N<sub>2</sub>H<sup>-</sup> anion could be used as tracer of nitrogen in the ISM and in media where N<sub>2</sub> is abundant (e.g. Titan atmosphere).