### 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 H₂. We report the first collisional data for an interstellar anion, the rate coefficients for the rotational excitation of CN⁻ by H₂. Rotational rate coefficients were calculated for temperatures ranging from 5 to 100 K. The CN⁻ 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 global potential energy surface and the bound states of the N₂H⁻ 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 N₂H⁻ complex.

### Rotational excitation of CN⁻ by H₂

The potential energy surface [1] was calculated within the supermolecular approach using a CCSD(T) method. In all calculations, to determine the interaction potential \( V(R, \theta, \phi) \), 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⁻ and H₂ centers of mass.

![Fig. 1: Body-fixed Jacobi coordinates of CN⁻–H₂.](image1)

The global minimum of the \( V(R, \theta, \phi) \) PES is located at \( R = 6.38 \) bohr for the collinear CN⁻–H₂ geometry \( \theta = 0, \phi = 0 \) with a well depth of 87.4 cm⁻¹. The depth of this well comes from the charge interaction with quadrupole and higher moments of the H₂ molecule and other induction or dispersion terms. Figure 2 represents the cut of the PES for \( \theta = 0^\circ \) and \( \phi = 0^\circ \).

![Fig. 2: Contour plot of the CN⁻–H₂ PES for the H₂ orientation corresponding to the minimum energy.](image2)

The CO molecule is isoelectronic with CN⁻ and has the same ground electronic state \( \Sigma^\text{+}. \) Hence, we compare in Fig. 4, on a small data sample, the temperature variation of the de-excitation rate coefficients of CN⁻ in collisions with para-H₂ (j₂ = 0) and ortho-H₂ (j₂ = 1). One can see that there are no significant differences between the collisions with both species of H₂. It is interesting to note that for collisions with both para- and ortho-H₂, inelastic rate coefficients with \( \Delta j_2 = 1 \) are larger than those with \( \Delta j_1 = 1 \).

![Fig. 3: Temperature variation of collisional de-excitation rate coefficients of CN⁻ by H₂. Panel a) para-H₂ (j₂ = 0) and Panel b) ortho-H₂ (j₂ = 1).](image3)

The CO molecule is isoelectronic with CN⁻ and has the same ground electronic state \( \Sigma^\text{+}. \) Hence, we compare in Fig. 4, on a small data sample, the temperature variation of the de-excitation rate coefficients of CN⁻ in collisions with H₂ (j₂ = 0) with those obtained recently for the neutral CO molecule in collisions with H₂ (j₂ = 0). On can clearly see that the CN⁻ rate coefficients are significantly larger than those of CO. Indeed, the CN⁻–H₂ (j₂ = 0) rate coefficients are up to a factor of ten larger than the one of CO–H₂ (j₂ = 0).

![Fig. 4: Temperature variation of the CN⁻ (solid lines) and CO (dashed lines) de-excitation rate coefficients for collisions with para-H₂ (j₂ = 0).](image4)

The large difference can be explained by the shape of the PES. The well depth of the CO–H₂ PES is 93 cm⁻¹ whereas the one of CN⁻–H₂ PES is 875 cm⁻¹ 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.

### N₂H⁻: a new interstellar anion?

The N₂H⁻ 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 MRCl approach. A large diffuse basis set of aug-cc-pVQZ quality is used for the description of the nitrogen and hydrogen atoms. The present work uses a Jacobi coordinate system, in which \( \nu \) is the N₂ interior distance, \( R \) is the distance from the center of mass of N₂ to the H⁻ atom and \( \theta \) the angle between the two distance vectors.

![Fig. 5: ICASSCF/aug-co-pVQZ cuts of the ground 3D PES of N₂H⁻ by H₂.](image5)

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 N₂H⁻ complex.

![Fig. 6: Contour plot (in cm⁻¹) of PES of the N₂H⁻ system as a function of Jacobi coordinates \( R \) and \( \theta \). The bond length is held fixed to 2.08 bohr.](image6)

### Conclusion

The CN⁻–H₂ 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⁻ emission lines observed with current and future telescopes [4]. The N₂H⁻ complex could be used as a tracer of the H⁻ ion in ISM, which presence was suggested but never established. More interestingly, the stable N₂H⁻ anion could be used as tracer of nitrogen in the ISM and in media where N₂ is abundant (e.g. Titan atmosphere).