

Frequency-Dependent Polarizability of an H^- Anion

A S KORNEV¹, V E CHERNOV¹, B A ZON¹, P KUBELÍK², AND M FERUS²

¹Voronezh State University, Voronezh, Russia

²J Heyrovský Institute of Physical Chemistry of the Czech Academy of Sciences, Prague, Czech Republic

Contact Email: a-kornev@yandex.ru

The simplest anion H^- is very important for both science and technology. Particularly, it is used to test theoretical methods for describing more complex systems and is involved in the formation of the spectra of stars and the Sun. The frequency-dependent polarizability (FDP) of anions is their most important characteristic, which determines the rates of various photoprocesses, as well as the cross-section of polarization bremsstrahlung. The corresponding results are used to describe some processes in the solar chromosphere.

In [1], the results of early calculations of the FDP of the H^- anion by various methods known at that time were presented, indicating the error bar. In [2], the FDPs were found using model potentials by the Dalgarno – Lewis method. Finally, in a recent paper [3], the polarizabilities were calculated by the summation-over-pseudostates method using variational wave functions with a random distribution of parameters.

In figure 1, we present the results of *ab initio* CCSD calculations of dipole FDP in the ground state of H^- using the quantum-chemistry NWChem package. The non-standard correlation-consistent Gaussian x-aug-cc-pV6Z basis sets of quality 6 with $x = 3$ (t) or 4 (q) diffuse functions for each orbital were involved. We have explored the entire frequency range up to the single-photon detachment threshold. There is an acute sensitivity of the FDP to the choice of the number of diffuse functions x in comparison with the affinity energy, which for quality higher 5 is practically independent of x . The results obtained in this research by the CCSD method for $x = 4$ agree with the data from [3] with an accuracy of 0.15% and fit into the error bar found in [1] over the entire frequency range.

In [4], the DFT methods with aug-cc-pVXZ basis sets of quality $X = 5$ or 6 also showed high efficiency in the calculations of the FDPs of neutral diatomic molecules. However, for H^- and $x = 1$ or 2 (d), the DFT methods underestimates the results from [3] by 2 – 6 times due to the low binding energy of the optical electron and, as a consequence, the large size of the anion (~ 4.5 Bohr). At present, the use of highly diffuse basis functions does not seem to be implemented in quantum-chemistry DFT methods. Moreover, these methods give the E_A that differs by 15% from the tabulated value. Thus, the role of the diffuseness parameter of the cc basis set in calculations of the FDP of anions is very important.

Acknowledgements: This research was supported by the RFBR (19-52-26006) and by the GAČR (20-10591J).

References

- [1] R M Glover and F Weinhold, J. Chem. Phys. **65**, 4913 (1976)
- [2] P A Golovinskii and B A Zon, Opt. Spectrosc. **45**, 733 (1978)
- [3] S Kar, Y-S Wang, Y Wang and Y K Ho, Int. J. Quantum Chem. **118**, e25515 (2018)

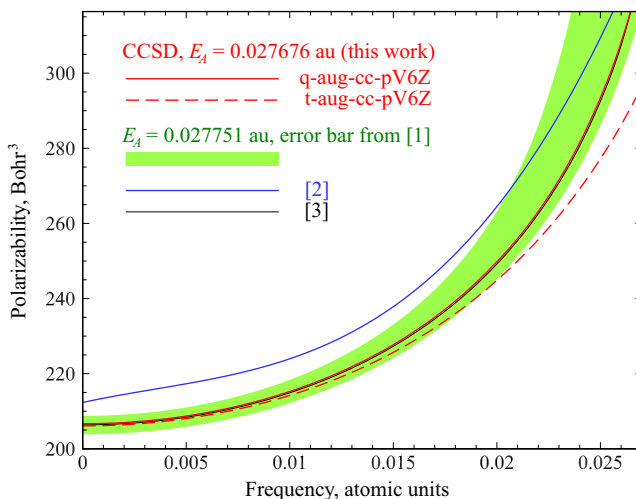


Figure 1: Frequency-dependent polarizability of a H^- anion calculated with some methods. The tabulated value of affinity energy is $E_A = 0.0277165$ au (0.75 eV)

[4] A S Kornev, K I Suvorov, V E Chernov and B A Zon, Chem. Phys. Lett. **711**, 42 (2018)