

Collision-induced spectra of oxygen and nitrogen molecules

Tijs Karman², Gerrit C. Groenenboom¹, Ad van der Avoird¹

1) *Theoretical Chemistry, Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands*

2) *Department of Chemistry, Durham University, South Road, Durham DH1 3LE, United Kingdom*

Collision-induced absorption is the phenomenon that interactions between colliding molecules lead to absorption of light, even for transitions that are forbidden for the isolated molecules. Collision-induced absorption contributes to the atmospheric heat balance and is important for the electronic excitations of O₂ that are used for remote sensing. Absorption by O₂-O₂ pairs has been put forward as a biomarker to be observed in exoplanetary transit spectra.

First, we studied the roto-translational spectrum of N₂-N₂ collision complexes using quantum mechanical line-shape calculations [1, 2]. Apart from some work on effectively isotropic systems such as H₂-H₂ and H₂-He, such calculations have always been performed with the approximation that the interaction potential between the colliding molecules is isotropic. We developed a scattering approach by which we could fully include the interaction anisotropy and we demonstrated that this anisotropy increases the line strength and brings our calculations in closer agreement with experimental spectra.

Next, we performed an ab initio study of the X ³Σ_g⁻ → a ¹Δ_g and X ³Σ_g⁻ → b ¹Σ_g⁺ electronic transitions of O₂, which are electric-dipole forbidden by both spin and spatial selection rules [3–5]. We unambiguously identified the underlying absorption mechanism, which—contrary to textbook knowledge—is shown to depend explicitly on the collision partner: N₂ or O₂. This explains experimentally observed qualitative differences between O₂-O₂ and O₂-N₂ collision-induced spectra in the overall intensity, line shape, and vibrational dependence of the absorption spectrum. Moreover, we provided explicit analytical expressions for the spectral line shape depending on the underlying mechanism, which can be applied in the calibration of satellite spectrometers that probe various gases in the atmosphere.

[1] T. Karman, A. van der Avoird, and G. C. Groenenboom, *J. Chem. Phys.* 142, 084305 (2015).

[2] T. Karman, E. Millordos, K. L. C. Hunt, G. C. Groenenboom, and A. van der Avoird, *J. Chem. Phys.* 142, 084306 (2015).

[3] T. Karman, A. van der Avoird, and G. C. Groenenboom, *J. Chem. Phys.* 147, 084306 (2017).

[4] T. Karman, A. van der Avoird, and G. C. Groenenboom, *J. Chem. Phys.* 147, 084307 (2017).

[5] T. Karman, M. A. J. Koenis, A. Banerjee, D. H. Parker, I. E. Gordon, A. van der Avoird, W. J. van der Zande, and G. C. Groenenboom, *Nature Chem.* 10, 549 (2018).

Spectroscopy of Molecular Radicals in Helium Droplets

PT2:

Gary Douberly

University of Georgia, Athens, Georgia, United States

Catalytic thermal cracking of O_2 is employed to dope helium droplets with $O(^3P)$ atoms.^[1] Mass spectrometry of the doped droplet beam reveals an O_2 dissociation efficiency larger than 60%; approximately 26% of the droplet ensemble is doped with single oxygen atoms. Sequential capture of $O(^3P)$ and HCN leads to the production of a hydrogen-bound O–HCN complex in a 3S electronic state, as determined *via* comparisons of experimental and theoretical rovibrational Stark spectroscopy. *Ab initio* computations of the three lowest lying intermolecular potential energy surfaces reveal two isomers, the hydrogen-bound (3S) O–HCN complex and a nitrogen-bound (3P) HCN–O complex, lying 323 cm^{-1} higher in energy. The non-relativistic HCN–O to O–HCN interconversion barrier is predicted to be only 42 cm^{-1} . Moreover, the barrier is reduced upon explicit consideration of spin–orbit coupling. Consistent with the prediction of a relatively small interconversion barrier, there is no experimental evidence for the production of the nitrogen-bound species upon sequential capture of $O(^3P)$ and HCN.

[1] Brice, J. T.; Franke, P. R.; Douberly, G. E. *J. Phys. Chem. A*, **2017**, 121, 9466.