Spectra of O_2 induced by collisions with N_2 and O_2

Tijs Karman[a,b], Gerrit C. Groenenboom,[a] and Ad van der Avoird[a]

[a] *Theoretical Chemistry, IMM, Radboud University, Nijmegen, The Netherlands*
[b] *Present address: Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA, USA*
A.vanderAvoird@theochem.ru.nl

Collision-induced absorption (CIA) is the phenomenon that light is absorbed through the interaction between colliding molecules, even for transitions that are forbidden for the isolated molecules. CIA contributes to the atmospheric heat balance and is important for the electronic excitations of O_2 that are used for remote sensing. Moreover, absorption by O_2-O_2 pairs has been proposed as a biomarker to be observed in exoplanetary transit spectra.

The absorption spectra of the $X\,^3\Sigma_g^- \rightarrow a\,^1\Delta_g$ and $X\,^3\Sigma_g^- \rightarrow b\,^1\Sigma_g^+$ electronic transitions in O_2 are extremely weak, since these transitions are electric-dipole forbidden by both spin and spatial selection rules. Important additional absorption is induced by collisions with N_2 and O_2. We computed the O_2-O_2 and O_2-N_2 CIA spectra by *ab initio* electronic structure calculations of the relevant ground and excited state interaction potentials and the transition dipole moment functions, followed by diabatization and quantum mechanical scattering calculations [1,2,3]. We unambiguously identified the underlying mechanisms, which —contrary to textbook knowledge— are shown to depend explicitly on the collision partner: N_2 or O_2. This explains experimentally observed qualitative differences between O_2-O_2 and O_2-N_2 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 greenhouse gases or pollutants in the atmosphere [4].

References

1. T. Karman, A. van der Avoird, and G. C. Groenenboom, *J. Chem. Phys.* **147** (2017), 084306.
2. T. Karman, A. van der Avoird, and G. C. Groenenboom, *J. Chem. Phys.* **147** (2017), 084307.
3. 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** (2018), 549.
4. T. Karman, I. E. Gordon, A. van der Avoird, Y. I. Baranov, C. Boulet, B. J. Drouin, G. C. Groenenboom, M. Gustafsson, J.-M. Hartmann, R. L. Kurucz, L. S. Rothman, K. Sun, K. Sung, R. Thalman, H. Tran, E. H. Wishnow, R. Wordsworth, A. A. Vigasin, R. Volkamer, and W. J. van der Zande, *Icarus*, **328** (2019), 160.