



Collision induced absorption in molecular oxygen between 670 and 950 nm

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Molecular oxygen is used in satellite retrievals for the determination of surface pressure, temperature and cloud height. Oxygen also influences atmospheric chemistry both in its ground and in its excited states. In both cases, optical transitions between the ground – $X^3\Sigma_g^-$ –state and the next two lowest state – $a^1\Delta_g$ and $b^1\Sigma_g^+$, play an important role. These transitions are weak, requiring path lengths of kilometers to be observed.

During a collision, the transition probability is enhanced. Unfortunately, accurate predictions are not available to describe the resulting absorptions. As such, we measured, using cavity ring-down, the collision induced absorption (CIA) related to two bands resulting from the $b \leftarrow X$ transition, the A-[1,2] and B-bands [3], and the previously unobserved band of the $a(v=2) \leftarrow X(v=0)$ transition.

For the A- and B-band the normal, non-collisionally enhanced, transition contributes and dominates. In order to retrieve the CIA in these regions, we measured in between the lines. We corrected for the absorption strength using Voigt line shapes in combination with line mixing.

In the region of the X-a transition the effect of the normal line absorption is negligible in comparison to the collision induced component. However, the CIA is strong enough to give a measurable transition probability (order of $5.10^{-8} \text{ cm}^{-1}$ at 1 Bar of oxygen). Although a weak feature on the level of our atmosphere, the CIA enhancement is stronger than *a priori* expected.

Furthermore, the influence of nitrogen as collision partner was studied for the A-band and the X-a transition. Here we report that the effect of collisions between oxygen molecules is very different from oxygen-nitrogen collisions, for reasons yet unknown.

Also, for all the regions, we find that Rayleigh scattering is non-negligible. Because of the linear pressure dependence of Rayleigh scattering on pressure, we can deduce its strengths experimentally even below these transitions. The strengths correspond well with theoretical results.

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[2]: Frans R. Spiering, Maria B. Kiseleva, Nikolay N. Filippov, Bas van Lieshout, Adriaan M.H. van der Veen and Wim J. van der Zande, Molecular Physics, **109**, 2011, 535–542

[3]: Frans R. Spiering, Maria B. Kiseleva, Nikolay N. Filippov, Line van Kesteren and Wim J. van der Zande, Phys. Chem. Chem. Phys., **13**, 2011, 9616–9621