Atomic and molecular interactions in dilute media

(Michael Chrysos, Florent Rachet)

The principal mission of our group is the study of collision-induced processes by compressed non-polar atomic or molecular gases. Its know-how covers both experimental and theoretical aspects. As far as the experiment is concerned, our Raman-scattering equipment is so sensitive that makes it possible the detection of light fluxes as tiny as of a few photoelectrons per week. To give an equivalent of what such a weak signal means, the light captured on Earth's surface by a candle burning on the Moon is a tangible example. As for theory, our group develops novel approaches, mostly quantum, whose aim is the study of Raman-scattering- or IR-absorption-relevant induced spectra. Both types of processes directly bring into the play the interactions between the particles of the medium. Owing to their strong collective character and to the weak signals they generate, such interactions are a challenge for detection and for theory. These interactions have a major role in many physical phenomena, and especially in the greenhouse effect of some planetary atmospheres. More particularly, their significance in the physics of carbon dioxide and of methane is all but negligible. As has been shown by our recent results[1,2], vibrational modes that are infrared-absorption-inactive in those molecules, can contribute substantially to the absorption by these gases, owing to the interactions between the gas molecules. Through our studies, the whole topic of the collision-induced phenomena has enjoyed a renewal of interest in recent years. The role of the collisions in the interception, absorption and scattering of photons, which had thus far only partially been understood and largely underestimated (especially in environments that are hot and dense in CO_2 or CH_4) garnered global media attention, and it was highlighted by the international press.

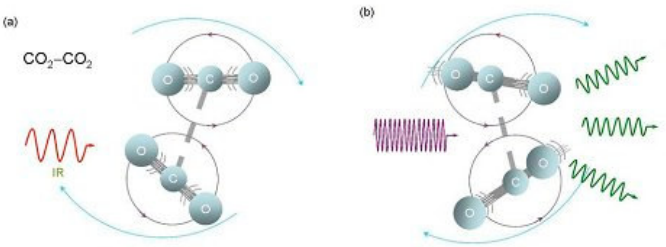

Fig. 1. Colliding CO_2 molecules that capture a photon during the collision. Each molecule rotates around itself and vibrates in one of its normal modes. (a) Because of the collisions, the absorption of photons becomes possible even if the two molecules vibrate in modes that are absorption-inactive (symmetric stretching mode). (b) Scattering of a visible-color photon by a molecular pair. The two molecules vibrate in their stretching asymmetrical mode, which is Raman-inactive.

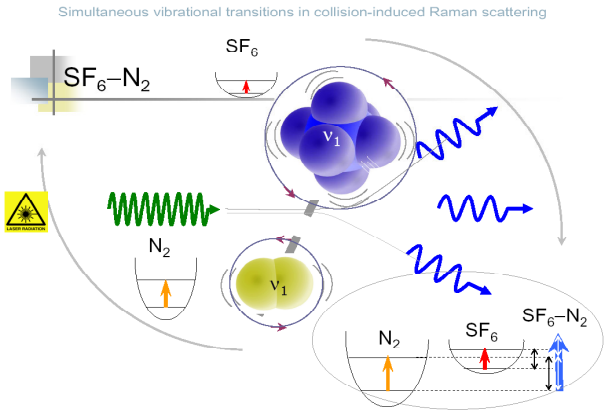

Fig. 2. Double vibrational transition in Raman scattering by gaseous mixture SF_6-N_2

Among induced spectral bands, the study of the so-called double vibrational transitions[3,4] is a hot and timely subject, and a challenge for experiment and theory. Their bands are fingerprints of two transitions occurring simultaneously in two interacting molecules, and for this reason their signals are far weaker than those generated by standard collision-induced processes. Such unstructured bands are suspected of being actors in atmospheric processes. To see these signals, we use gas mixtures rather than pure gases. In so doing, this "double process", so unlikely, takes place in spectral regions that are totally free from any spectral signature due to the individual molecules. We have already observed and analyzed such transitions within gaseous mixtures of greenhouse molecules and inert ones (SF_6-N_2, CH_4-N_2).

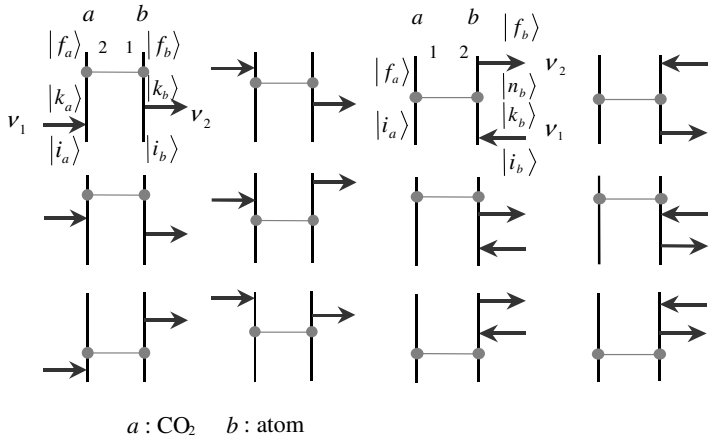

Fig. 3. Graphs involved in our novel diagrammatic approach. The six graphs at the left illustrate half of the possibilities that are relevant to the so-called dipole-induced quadrupole mechanism. The remaining half can be obtained from the previous half by simply changing the orientation of the vectors (photons). The six graphs at the right side of the picture show all the possibilities, which are relevant to a new nonlinear mechanism that we discovered.

As far as atomic gases are concerned[5,6], gas mixtures[7,8] had never been studied with Raman spectroscopy until our recent works. In fact, in a way analogous to a molecular pair, atomic pairs can also generate isotropic or anisotropic spectra, and such signatures can indeed be revealed by our equipment. These spectra originate in the two invariants of the induced-polarizability tensor, $\Delta\alpha$. The induced-polarizability, which is defined as the difference between the polarizability of a pair of particles and those of the two independent units, depends on the separation between the particles. Its knowledge determines many macroscopic quantities such as the dielectric virial coefficient, the refractive index and the Kerr constant. Our experimental results are compared with quantum calculations. These calculations employ sophisticated numerical procedures that are also developed in our group. For instance, a novel spectral inversion method has been developed which makes it possible to overcome shortcomings in the existing models that are pinpointed through straightforward comparison between theory and experiment.

Furthermore, a general diagrammatic theory has been developed to describe collision-induced properties[9]. This theory, which involves arbitrary numbers, *M* and *N*, of molecule-molecule couplings and of photon-molecule couplings, is a significant extension of existing nonlinear-optics graphical theories since it makes it possible to exhaustively describe the induced polarization mechanisms. There, molecules are treated fully quantum-mechanically while electromagnetic fields are implicitely quantized via second quantization in a non-relativistic regime. With our theoretical development, processes that are as different as the collision-induced absorption, the collision-induced Raman scattering, or its nonlinear counterpart called hyper-Raman collision-induced scattering, can be viewed and studied as particular cases $N = 1$, 2, or 3, respectively, through instructive examples. The ensuing results reveal new mechanisms. Due to the lack of data, these mechanisms had so far been overlooked for decades.

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