Collisional dephasing of coherent molecular rotation in gases.

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The rotational coherence spectroscopy (RCS) is the Dopler-free time resolved polarization-sensitive technique for determining the main moments of inertia of molecules, structures of van-der-Waals complexes of polyatomic molecules and various species, and also for defining directions of the absorption and emission dipole moments in the molecular frame [1]. In the RCS, one measures the so called rotational recurrences (RRs) which look like (quasi)periodic oscillations.

First, I would like to make a brief introduction into the subject of the RCS and to sum up the results of our recent semiclassical studies of RRs in ensembles of isolated asymmetric top molecules [2]. This includes a comprehensive classification (by period and polarity) of different RRs and prediction of new kinds of transients.

Second, I intend to clarify the question of how intermolecular collisions influence the RR decay. Our mane findings can be formulated as follows [3]:

(I) Collisions do not change the RR period.

(II) The time decay of the RR signal is uniquely determined by the rotationally invariant cross-sections $\sigma^{\lambda}(j, j_1, j, j_1)$ (which describe broadening of individual lines in rotationally resolved spectra) and $\sigma^{\lambda}(j, j, j', j')$ (which govern collisional relaxation of state multipoles).

(III) The RRs are strongly damped by those collisions that substantially change the magnitude of the angular momentum. On the contrary, the RRs are less affected by those collisions that (at least partially) preserve the magnitude of the angular momentum and result primarily in the change of its direction. The width and form of the rotational transients is also collision dependent.

(IV) It is convenient to analyze the collisional decay of the RRs in terms of the envelopes of the RR signals and the corresponding integral relaxation times. These quantities are demonstrated to be very useful for getting knowledge about the collision dynamics. In addition, one can safely calculate these quantities by treating the rotational motion semiclassically.

(V) Collisions, either weak or strong, do partially preserve the rotational coherency, and a useful information about the efficiency of the angular momentum change due to collisions can be extracted from the RR time decay.

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[2] M.F. Gelin, V.A. Tolkachev, A.P. Blokhin. Chem. Phys. 255 (2000) 111.
[3] A.P. Blokhin, M.F. Gelin, T. Dreier. Phys. Chem. Chem. Phys. 1 (1999) 5583.