Nonlinear Collision Shifts of Alkali 0-0 Hyperfine Transitions Due to Van der Waals Molecule Formation

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As illustrated in Fig. 1, the frequency stability of vapor-phase atomic clocks at 10^4 seconds averaging time is pushing into the 10^{-16} frequency stability region. At such levels, vapor-phase atomic clocks would no longer contribute to the signal-in-space user-range-error of global navigation satellite systems [1], and systems of such clocks might be employed for fundamental physics [2].

Achieving that goal, however, will require a renewed attack on our understanding of the perturbations affecting atomic structure: we will need to carefully validate our theoretical understanding of the ac-Stark shift [3]; we will

Figure 1: Allan deviation at 10^4 seconds for vapor-based atomic clocks as a function date.

need to more fully understand the role of mesoscopic physics on measurements of atomic structure [4], and we will need to reanalyze the influence of collisions shifts to ensure we fully understand the manner in which variations in the perturbation might give rise to frequency instability.
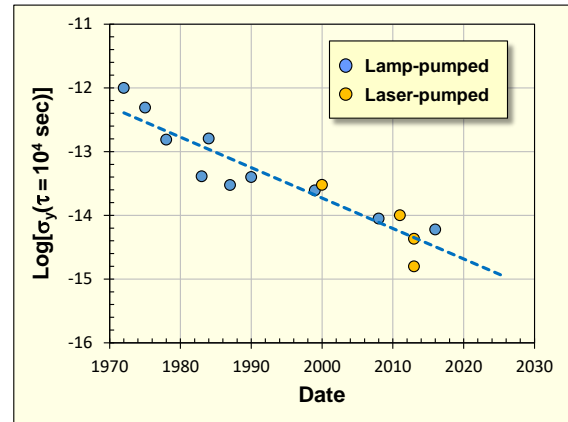
Here, we present a theory of Van der Waals molecule collision-shifts for the 0-0 hyperfine transition in alkali/noble-gas systems. We describe the effect as arising from three fundamental interactions: 1) a change in the alkali valence-electron's density at the nucleus, 2) an interaction of the alkali valence-electron's spin with the rotational angular momentum of the Van der Waals molecule, and 3) a mixing of p-wavefunction character into the alkali valence-electron's ground state. This later gives rise to a change in the hyperfine dipole-dipole interaction, and the appearance of a hyperfine quadrupole interaction, which is sensitive to the nucleus' electric quadrupole moment. After accounting for systematic effects in the measurements at high buffer-gas pressures (where the transition from optical inhomogeneous Doppler broadening to homogeneous pressure broadening takes place), we find very good agreement between theory and ^{85}Rb/Xe and ^{87}Rb/Xe nonlinear collision shift measurements.

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3. F. Levi, J. Camparo, B. Francois, C. E. Calosso, S. Micalizio, and A. Godone, *Precision test of the ac-Stark shift in a rubidium atomic vapor*, Phys. Rev. A 93, 023433 (2016).

4. A. Hudson and J. Camparo, *Mesoscopic physics in vapor-phase atomic systems: Collision-shift gradients and the 0-0 hyperfine transition*, Phys. Rev. A 98, 042510 (2018).