**Vibration-Rotation Coupling Dynamics of Laser Induced Nonadiabatic Molecular Alignment**

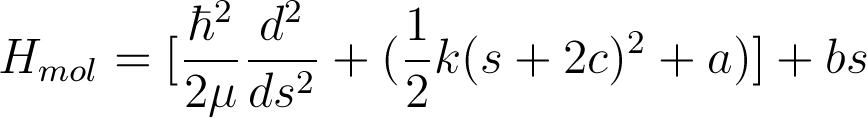
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Within a variety of experimental premises novel to an interdisciplinary array of sciences, control of molecular alignment within a medium is essential. Chemical reaction dynamics, manipulation of stereochemistry, molecular structure, quantum information processing, and dissipative media properties all interface with the problem of maintaining spatial control of individual molecules without disrupting the underlying physics of the scenario. My scientific studies at Northwestern University, emphasizing the application of physics to interdisciplinary science, have fascinated me with the problem this poses. I wish to use my research background to pursue extending rotational control of molecular alignment through the application of short, intense laser pulses to a more fundamental model that simultaneously encompasses vibrational modes of activity.

The nonadiabatic alignment of linear molecules has been rigorously studied as a fundamental physics problem1. A laser pulse of short duration relative to the rotational parameters of the subject molecule upon which it is incident will impart a large amount of angular momentum to the system. This leaves a coherent superposition of aligned rotational states. Following laser pulse turn-off, this system will continue to exhibit periodic reoccurrences of strong rotational alignment on a timescale dictated by the inertial properties of the molecule. Adjustment of the parameters of the laser used can, in fact, strengthen the post-laser alignment revivals beyond what was achieved in the presence of the optical field, and is thus a highly relevant technique for field-sensitive experimental conditions. Much of my undergraduate research at Northwestern University has considered extensions of this premise by modifying molecular rotational degrees of freedom to study effects on single-molecule behavior. This model, consistent with others in the field, was predicated on the assumption that the effects of vibration-rotation coupling were negligible. Under the timescales considered, this was a valid assumption. As nonadiabatic alignment is extended to more physical systems, however, the importance of vibrational activity increases and this assumption no longer holds.

I wish to address the fundamental question of the effects of allowing vibration-rotation coupling within an alignment system, and exemplify the physical consequences of this effect by considering its application within the context of a dissipative medium. I will complete this work at JILA working with Dr. Andreas Becker. To simulate the coupled vibration-rotation system, I will solve the time-dependent Schrödinger equation for a rotating and vibrating diatomic molecule. Vibration and vibration-rotation coupling can be introduced to the rigid rotor model molecular Hamiltonian by incorporating two additional terms from the power series expansion of the effective potential of the system describing the radius-dependent chemical bonding2. It is sufficient and computationally desirable to approximate the vibrational potential to have the shape of a harmonic function so long as vibrational activity is confined within a small number of vibrational states. This is allowed for by preparing the molecule initially at the ground state, with the expectation that interaction with the laser source will not cause significant activation of high-energy vibrational states. I note, however, that anharmonic vibrational behavior can better approximated using the Morse potential if necessary2.

With these considerations, the molecular Hamiltonian becomes:



where µ denotes the reduced mass of the molecule, *k* is a constant dictating harmonic motion, and *s* denotes radius length change from the ground state value *r0*. The values *a, b,* and *c* come from the expansion of the effective potential, and are associated with the molecular rotational constant *B0*and the rotational quantum state *J* as: , , and . This final *c* term is what ultimately gives rise to vibration-rotation coupling, and yields vibrational frequencies that are proportional to *J*.

To describe the interaction of the molecule with linearly polarized light, another term controlling the interaction of the molecular induced dipole with the laser must also be added. Equation 7 in Ref. 1 describes the shape of this contribution, but as this is common to the literature, I leave it to the reference to demonstrate its derivation. With this total Hamiltonian, we are prepared to proceed with solving the time dependent Schrödinger equation. Expansion of the wavefunction into a basis of coupled spherical harmonic functions and normalized Hermite polynomials yields a set of coupled differential equations for the values of the constants of expansion. Solution of this set of equations then yields the vibrational-rotational wavefunction, from which the expectation values of observables of interest may be calculated. In particular, one may calculate the rotational alignment achieved by molecules in the system over an extended period of time, to observe the effects of energy transfer between rotational and vibrational states. While the laser pulse is expected to act only to excite rotational states, I hypothesize that the coupling into the vibrational system will periodically diminish and enhance free-field rotational alignment characteristic of the constant controlling this coupling.

After establishing this model, I wish to study it within context of alignment within dissipative media. While vibrational relaxation has long been used as a source of information regarding material properties, recent activity in gas-phase experiment3 and theory4 have explored the potential of laser-induced rotational alignment in dissipative systems. The role of vibration-rotation coupling in dissipative media promises to explore the interface of these studies in a way that will provide elucidation regarding how medium properties effect energy transition between vibrational and rotational states. It will also test the ability of media properties to enhance alignment or extend rotational alignment duration through these energetic couplings.

Dr. Becker’s previous theoretical studies on the coherent control of chemical reactions and the imaging of molecular dynamics forms a natural ground work for studies extending laser control to molecules in dense media. In particular, it welcomes future analyses using ultra-fast imaging techniques to observe more closely the implications of molecular control in dissipative media for correlated electron motion. Dr. Becker’s close work with the Kapteyn-Murnane group at JILA provides for opportunities for experimental testing of the developed theory. Exploring vibrational-rotational coupling of dipole molecules in the context of alignment systems is a necessary next step to improve models of this process. The unique control nonadiabatic alignment affords to molecular alignment in systems sensitive to strong external fields makes it a system of both fundamental and applied interest, and I would like to dedicate the next step of my research career to exploring the implications of this phenomenon.

**References:**

1. Seideman, T., Hamilton E. *Advances in Atomic, Molecular and Optical Physics* **2006**, *52, 289-329.*
2. Mueller, M. *Fundamentals of Quantum Chemistry*, Kluwer Academic/Plenum Publishers, New York, 2001; pp. 115-136. ISBN 0-306-46596-5.
3. Vieillard, T., Chaussard, F., et al. *Journal of Raman Spectroscopy* **2008**, *39, 694-699.*
4. Seideman, T, Ramakrishna, S. *The Journal of Chemical Physics* **2006**, *124, 034101.*