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Published in:
Journal of Chemical Physics

Link to article, DOI:
[10.1063/1.4922309](https://doi.org/10.1063/1.4922309)

Publication date:
2015

Document Version
Publisher's PDF, also known as Version of record

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Citation (APA):
Shu, C-C., & Henriksen, N. E. (2015). Communication: creation of molecular vibrational motions via the rotation-vibration coupling. *Journal of Chemical Physics*, 142, [221101]. <https://doi.org/10.1063/1.4922309>

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Citation: *The Journal of Chemical Physics* **142**, 221101 (2015); doi: 10.1063/1.4922309

View online: <http://dx.doi.org/10.1063/1.4922309>

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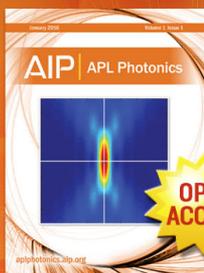
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Communication: Creation of molecular vibrational motions via the rotation-vibration coupling

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(Received 14 April 2015; accepted 28 May 2015; published online 8 June 2015)

Building on recent advances in the rotational excitation of molecules, we show how the effect of rotation-vibration coupling can be switched on in a controlled manner and how this coupling unfolds in real time after a pure rotational excitation. We present the first examination of the vibrational motions which can be induced via the rotation-vibration coupling after a pulsed rotational excitation. A time-dependent quantum wave packet calculation for the HF molecule shows how a slow (compared to the vibrational period) rotational excitation leads to a smooth increase in the average bond length whereas a fast rotational excitation leads to a non-stationary vibrational motion. As a result, under field-free postpulse conditions, either a stretched stationary bond or a vibrating bond can be created due to the coupling between the rotational and vibrational degrees of freedom. The latter corresponds to a laser-induced breakdown of the adiabatic approximation for rotation-vibration coupling. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4922309>]

Based on the assumption that the electronic, vibrational, and rotational degrees of freedom in a molecule can be separated from each other, concepts like the Born-Oppenheimer approximation (BOA),¹ vibrational normal modes,² and rigid-rotor approximation³ are all of paramount importance providing the fundamental framework for understanding molecular structure and dynamics. However, many physical and chemical processes deviate from these approximations due to the coupling between different degrees of freedom.⁴⁻⁷ The coupling between different molecular degrees of freedom plays a decisive role in many phenomena, including electron transfer and energy redistribution. A number of theoretical and experimental works have addressed either the electron-nuclear coupling beyond the BOA in nonadiabatic processes^{5,6,8} or the coupling between vibrational modes leading to intramolecular vibrational redistribution (IVR).⁹ A fundamental question remains unanswered: How the rotation-vibration coupling unfolds in real time after a pure rotational excitation? To that end, we present an examination following slow as well as fast pulsed rotational excitations.

The coupling between the rotational and vibrational degrees of freedom can be illustrated by the field-free Hamiltonian for the rotation-vibration motion of a diatomic molecule in the interatomic potential $V(R)$

$$\hat{H}_0 = -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} \right) + \frac{\hat{J}^2}{2\mu R^2} + V(R), \quad (1)$$

where μ is the reduced mass, R is the internuclear distance, and \hat{J}^2 is the squared angular momentum operator with eigenvalue

equation

$$\hat{J}^2 Y_{JM}(\theta, \phi) = J(J+1)\hbar^2 Y_{JM}(\theta, \phi), \quad (2)$$

where $Y_{JM}(\theta, \phi)$ denotes a spherical harmonic function depending on the spherical polar angles θ and ϕ , J is the rotational quantum number, and M is the magnetic quantum number. Since $[\hat{H}, \hat{J}] = 0$, the angular momentum is a constant of motion. The stationary states can (similar to the relative motion of the electron and proton in the hydrogen atom) be expressed as a product of a nuclear radial wave function $R_{nJ}(R)$ and the spherical harmonic function $Y_{JM}(\theta, \phi)$, i.e., $R_{nJ}(R)Y_{JM}(\theta, \phi)$, where n is the vibrational quantum number. To that end, it is noted that the wave packet associated with a non-stationary rotational state (i.e., a state which encompasses several J values) cannot be exactly factorized into a radial and an angular part.

Typically, in the electronic ground state, $V(R)$ has a deep sharp minimum at $R = R_e$, and a Taylor expansion of the centrifugal term around $R = R_e$ gives

$$\frac{\hat{J}^2}{2\mu R^2} = \frac{\hat{J}^2}{2I_e} \left[1 - \frac{2(R - R_e)}{R_e} + \frac{3(R - R_e)^2}{R_e^2} + \dots \right], \quad (3)$$

where $I_e = \mu R_e^2$ is the moment of inertia evaluated for $R = R_e$. Thus, $\hat{H}_0 = \hat{H}_{\text{vib}} + \hat{H}_{\text{rot}} + V_c$, where \hat{H}_{rot} is the first term in Eq. (3) corresponding to a rigid rotor and V_c denotes the subsequent coupling terms

$$V_c = \frac{\hat{J}^2}{2I_e} \left[-\frac{2(R - R_e)}{R_e} + \frac{3(R - R_e)^2}{R_e^2} + \dots \right]. \quad (4)$$

The modification of the rotational-vibrational energy levels introduced by the coupling V_c is well-known.¹⁰ These

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(typically small) additional terms described within time-independent perturbation theory lead to terms which are interpreted as (i) a centrifugal distortion which stretches the molecule when $J > 0$ (independent of the vibrational quantum number n) and (ii) a dependence of the moment of inertia on the vibrational state—leading to a coupling which depends on the vibrational n as well as the rotational J quantum numbers.

Current state-of-the-art experiments allow for an impressive control of the rotational state of molecules, e.g., leading to strong alignment or even orientation of molecules.^{11–17} Prior to and in parallel with the experimental demonstrations, a number of theoretical works have been published.^{18–26} The control of angular momentum includes the possibility of slow (adiabatic) or fast (non-adiabatic, sudden) pulsed rotational excitation where slow and fast are relative to the time scale of rotational motion.

Pulsed excitation creates a rotational wave packet which consists of a superposition of rotational states, and subsequently postpulse periodic field-free alignment/orientation can be observed. The physical basis for the orientation is the interference between even and odd J -states which have different parities with respect to inversion at the origin. For a plane-polarized laser field, the periodically appearing highly aligned or oriented states are parallel to the direction of the field.

Using these contemporary tools for the precise control of the angular momentum, we consider the implications of the rotation-vibration coupling from a time-dependent point of view. With appropriate laser excitation, one can switch on the effect of rotation-vibration coupling in a controlled manner, e.g., starting from $J = 0$ (no coupling). This is quite unique and not so for other types of coupling, e.g., the coupling between vibrational modes. The picture which is often suggested—based on time-independent perturbation theory—is that rotational excitation is leading to bond stretching. In the following, we will see how this unfolds in real time and in particular demonstrate that this picture is not always true.

Within the time-dependent self-consistent field (TDSCF) approximation,^{27,28} a useful first approximate description of the interplay between the rotational and vibrational degrees of freedom can be obtained. The time-dependent wave function is at all times represented by the approximate factorized form $\Psi(R, \theta, \phi, t) = \chi(R, t)\Phi(\theta, \phi, t)$ (exact for eigenstate at $t = 0$) where $\chi(R, t)$ is found as a solution to

$$i\hbar \frac{\partial \chi(R, t)}{\partial t} = (\hat{H}_{\text{vib}} + \langle \Phi(\theta, \phi, t) | V_c | \Phi(\theta, \phi, t) \rangle) \chi(R, t). \quad (5)$$

That is, the vibrational degree of freedom experiences an additional potential, i.e., V_c averaged over the rotational part of the wave function. After the rotational/angular excitation is over, this potential is readily found to be time-independent and proportional to the expectation value of the squared angular momentum. Thus, including the first term in V_c , linear in $(R - R_e)$,

$$\langle \Phi(\theta, \phi, t) | V_c | \Phi(\theta, \phi, t) \rangle = -\langle \Phi(\theta, \phi, t) | \hat{J}^2 | \Phi(\theta, \phi, t) \rangle \frac{(R - R_e)}{R_e I_e}, \quad (6)$$

and the dynamics becomes—within a harmonic oscillator description—equivalent to a harmonic oscillator with a displaced minimum. That is, it can be anticipated that the vibrational dynamics will depend on how fast this displacement is introduced, i.e., how fast the angular momentum is switched on.

To that end, we recall the adiabatic approximation (see, e.g., Ref. 29). This approximation is in molecular physics typically applied to the separation of electronic and nuclear motions (BOA): A slow gradual change of nuclear positions gives a slow change in the electronic Hamiltonian which implies that electrons adjust to the new nuclear positions in a smooth continuous fashion and stay in the same stationary state during nuclear motion. In the same way, it can be anticipated that a slow gradual change in the rotational state of a molecule gives a slow change in the Hamiltonian associated with the vibrational degree. On the other hand, a fast (sudden) change of the rotational state is expected to lead to non-adiabatic effects and breakdown of the adiabatic approximation.

In the following, we consider a numerical illustration where the diatomic HF molecule in its electronic ground state is excited by an intense plane-polarized pulsed non-resonant laser field with polarization parallel to z , see Fig. 1. The field-free Hamiltonian \hat{H}_0 is given by Eq. (1) and the interaction Hamiltonian within the electric-dipole approximation is described by²⁰

$$\hat{H}_{\text{int}}(t) = -\mu(R)\mathcal{E}(t)\cos\theta - \frac{\mathcal{E}^2(t)}{2}\{\Delta\alpha\cos^2\theta + \alpha_{\perp}\}, \quad (7)$$

where $\mu(R)$ is the permanent electric dipole moment (in the absence of an electric field), $\Delta\alpha = \alpha_{\parallel}(R) - \alpha_{\perp}(R)$ where $\alpha_{\parallel}(R)$ and $\alpha_{\perp}(R)$ refer to the parallel and perpendicular components, respectively, of the polarizability tensor. The interatomic potential, dipole moment, and polarizability of HF are found in the literature.^{31,32} The polarizability anisotropy at the equilibrium distance is about 1.23 a.u. The molecular wave function is obtained by the time-dependent quantum wave packet method.³⁰ Initially, the molecule is assumed to be in its vibrational and rotational ground states ($n = 0$ and $J = 0$). Due

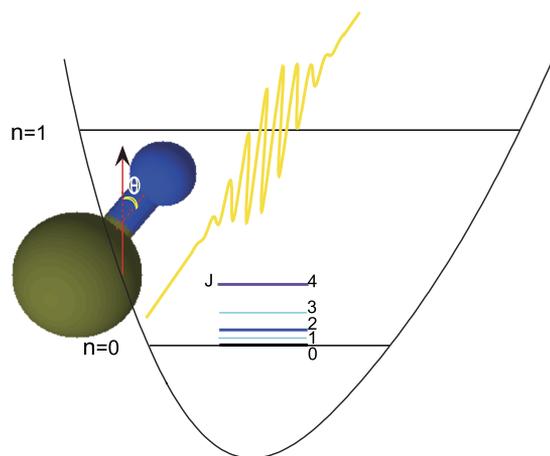


FIG. 1. Schematic illustration of the rotational excitation of the HF molecule in its electronic and vibrational ground states.

to the conservation of $M = 0$, the calculations can be restricted to two degrees of freedom (R, θ).

In a first simulation, we consider a slow rotational excitation of HF molecules excited by a train of seven nonresonant visible (vi) Gaussian profile laser pulses with a center frequency of $\omega_{vi} = 12\,500\text{ cm}^{-1}$ (i.e., $\lambda_{vi} = 800\text{ nm}$), a full-width at half-maximum (FWHM) of $\tau_{vi} = 100\text{ fs}$, and an intensity $I_{vi} = c\epsilon_0\mathcal{E}_{vi}^2/2 = 3.0 \times 10^{13}\text{ W/cm}^2$. The delay time between the pulses is fixed at $\Delta t = 268.5\text{ fs}$, which corresponds to the rotational period of a rotational wave packet which consists of the $J = 0$ and $J = 2$ rotational states of HF. Figure 2 shows the expectation value of the displacement $R - R_0$ and the distribution of rotational states after the interaction with each pulse. Here, $R_0 = \langle R \rangle_0 > R_e$ denotes the expectation value of the bond length in the vibrational and rotational ground states. The duration of the visible pulses was chosen to be substantially longer than the vibrational period ($\sim 8.25\text{ fs}$) and to ensure a selective rotational excitation. Results are shown for the real distance-dependent dipole moment and polarizabilities as well as for constant dipole moment and polarizabilities (corresponding to the values evaluated at the equilibrium bond distance). For constant values of the dipole moment and polarizabilities, no direct vibrational excitation is possible. Thus, a comparison of the two sets of calculation allows us to assess the extend to which selective rotational excitation is accomplished,

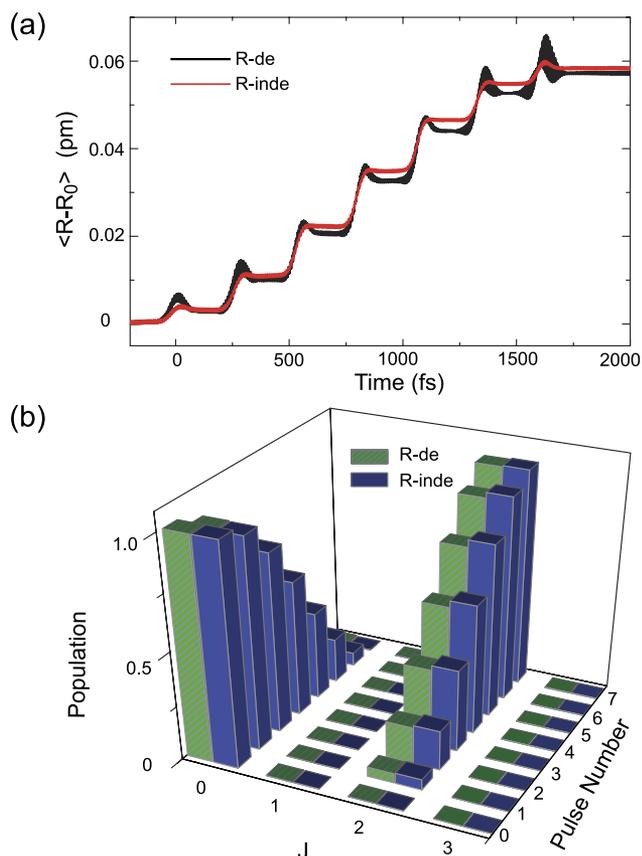


FIG. 2. (a) The expectation value of the displacement $R - R_0$ with a train of seven visible laser pulses and (b) the rotational population distribution after each pulse. The labels “R-de” and “R-inde” denote results where the dipole moment and polarizabilities are, respectively, dependent and independent of the bond length.

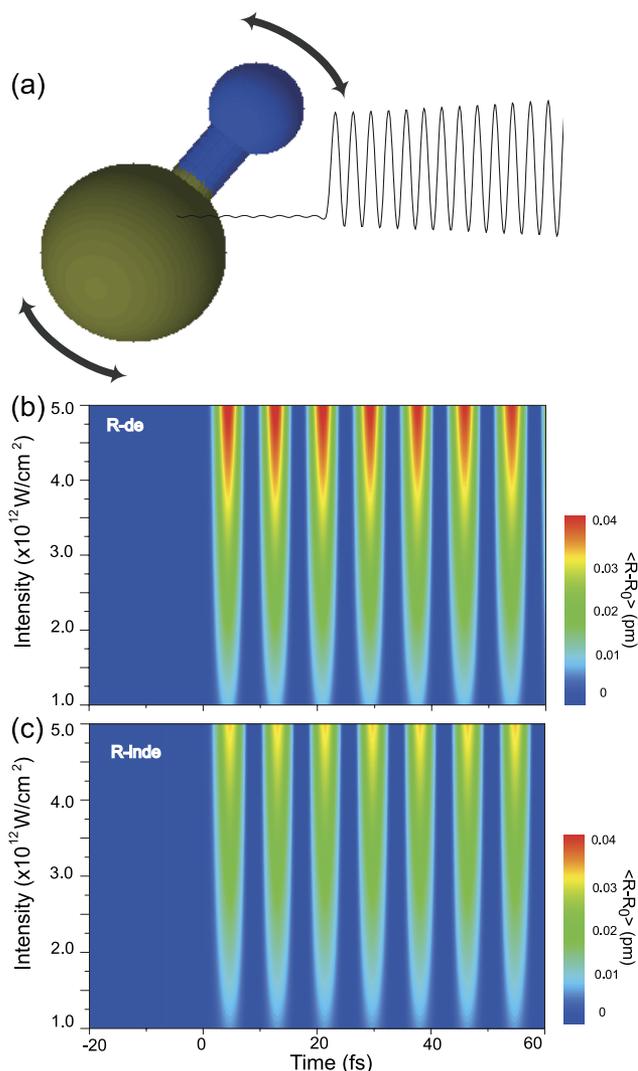


FIG. 3. (a) Schematic illustration of the fast rotational excitation of the HF molecule leading to non-stationary vibrational motion. The double arrows indicate rotational excitation and the oscillatory line is the expectation value of the bond length. (b) The expectation value of the displacement $R - R_0$ as a function of time and intensity of the ultra-broadband few-cycle IR pulse for the real distance-dependent dipole moment and polarizabilities as well as (c) for constant dipole moment and polarizabilities.

i.e., whether the change in the internuclear distance is due to the coupling between the rotational and vibrational degrees of freedom.

After the interaction with the visible laser pulses, a smooth increase in bond length is observed in Fig. 2(a), leading to new stationary stretched internuclear distances. The main difference between the results for the distance-dependent and distance-independent dipole moments and polarizabilities is a small transient bond stretching during the interaction with each laser pulse. Since the results with and without a distance-dependent interaction are very similar, the postpulse bond stretching is seen to be due to the coupling between the laser-induced rotational excitation and the vibrational degree of freedom. The rotational distribution changes from $J = 0$ to (essentially) $J = 2$, including superpositions of the two states, i.e., rotational wave packets between pulse 1 and pulse 7. In all cases, a smooth increase in bond length is observed after the

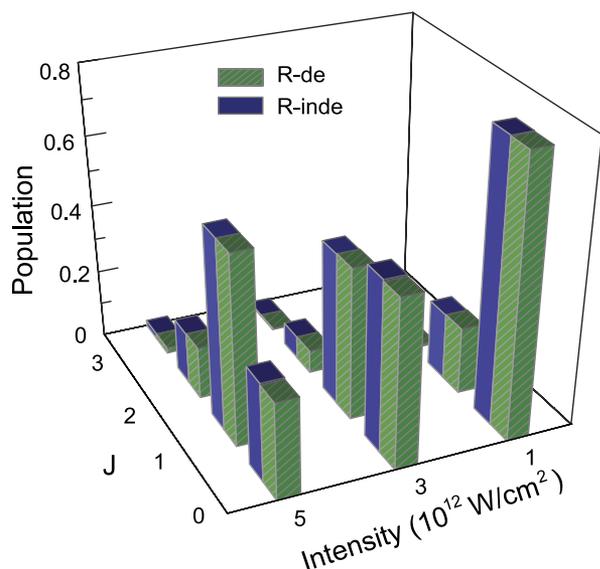


FIG. 4. The postpulse rotational population distribution at different intensities of the IR laser pulse for the real distance-dependent dipole moment and polarizabilities (“R-de”) as well as for constant dipole moment and polarizabilities (“R-inde”).

interaction with each pulse. Overall, the rotational excitation—and therefore the rotation-vibration coupling—is quite small, as shown in Fig. 2(b). These rotational excitations are due to the coupling via the molecular polarizability.

We now present results for a fast rotational excitation by using a single ultra-broadband few-cycle infrared (IR) Gaussian profile laser pulse with the FWHM of $\tau_{ir} = 5$ fs and a center frequency of $\omega_{IR} = 3300$ cm⁻¹ (i.e., $\nu_{IR} = 10^{14}$ Hz). This frequency is off-resonant with respect to the $\omega_{HF} = 4038$ cm⁻¹ vibrational frequency of HF and the duration of the IR pulse is similar to the vibrational period of HF (~8.25 fs). Figure 3 shows the expectation value of the displacement $R - R_0$ as a function of the intensity of the IR laser pulse. In all cases, the short IR pulse leads to non-stationary vibrational motion. The bond oscillates around a new bond distance which is larger than the original expectation value R_0 , and vibrational motion with the characteristic period of the HF molecule is observed. To gain insight into the underlying mechanism, Fig. 4 shows the distribution of rotational states with three different intensities of the IR pulse. The interaction with the IR pulse changes the rotational states by ± 1 and to a small extent by ± 2 . The change by ± 1 is due to the coupling via the permanent dipole moment. As the intensity increases, the rotational excitation to higher rotational states is enhanced, which increases the coupling between rotational and vibrational motions. Due to the large bandwidth of the pulse, some direct vibrational excitation takes place but when the possibility of a direct vibrational excitation is excluded, a qualitatively similar vibrational motion is observed in Fig. 3(c). Thus, a key point of this work is that rotational excitation is not always resulting in a stretched stationary chemical bond.

In summary, we have shown that a smooth increase in bond length can be accomplished via a slow (relative to the vibrational period) rotational excitation. This result is in accordance with the adiabatic theorem, i.e., a slow “forcing” of

the vibrational degree of freedom (via the rotation-vibration coupling) leads to an adiabatic change in the vibrational state. That is, starting from the vibrational ground state of $J = 0$, the molecule continues to stay in the instantaneous stationary vibrational ground state of higher rotational states. However, this picture fails when the rotational excitation is fast, where non-stationary vibrational motion is created via the rotation-vibration coupling. That is, a periodic vibrational motion in a molecule can be created by pure rotational excitation. This corresponds to a laser-induced breakdown of the adiabatic approximation for rotation-vibration coupling in molecules. We used simple laser pulses which can be generated with the current laser technology.

We illustrated these findings for the diatomic HF molecule; however, the universality of the results can be inferred from our analytical arguments. In the present work, the rotational excitation—and therefore the rotation-vibration coupling—and the resulting effect on the vibrational degree of freedom are quite small. Much stronger rotational excitation can, e.g., be accomplished via a so-called optical centrifuge.^{33–35} Furthermore, the selectivity of the pulsed excitation towards pure rotational excitation can be optimized by appropriate pulse shaping, e.g., obtained via optimal control theory.³⁶

This work was partially supported by the H. C. Ørsted Postdoctoral program of the Technical University of Denmark and the Vice-Chancellor’s Postdoctoral Research Fellowship program of the University of New South Wales, Australia.

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