

Fully Anharmonic Resonance Raman Spectrum of Diatomics Through Vibrational CI Calculations

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Abstract: Within the Born-Oppenheimer approximation, the pure vibrational Resonance Raman (RR) spectrum is obtained following three basic steps: (1) The Potential Energy Surface of the ground and one (or more) excited states must be calculated as well as the Electric Dipole Transition Moment Surface; (2) Vibrational energies and wavefunctions of those electronic states must be evaluated and (3) Building vibronic polarizabilities from the *sum over states* (current approach) or *time dependent* theory of the Raman effect. We present here a methodology to compute fully anharmonic RR spectrum of diatomic molecules where the potential energy curves (PEC) are evaluated using multiconfiguration *ab initio* wavefunctions and the vibrational problem is numerically solved using configuration interaction theory, where the matrix representation of the vibrational Hamiltonian is built using (hundreds/thousands of) harmonic oscillator basis sets. The potential energy contribution to that Hamiltonian matrix is numerically evaluated using the full PEC and cubic spline quadrature while the kinetic energy contribution is analytic. As an example, the RR differential cross sections of hydrogen molecule are presented in **Table 1**. The excitation laser wavelength is *109.12 nm*, corresponding to the CASSCF(124,2)/d-aug-cc-pVQZ wavelength of the electrically allowed $X^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+$ transition. A pure vibrational half-width at half-maximum $\Gamma = 6.01966 \text{ cm}^{-1}$, obtained after averaging the $B^1\Sigma_u^+$ fluorescence lifetimes over 25 rotovibronic states [1], was used to evaluate the RR polarizabilities. In general, the use of fully anharmonic wavefunctions results in a decrease of the predicted RR intensities of H_2 . Such behavior is also observed at the Franck-Condon level. In addition, a slower convergence of RR cross sections is observed when anharmonic vibrational wavefunctions are used to compute the RR intensities. There is also a change in the relative intensities when anharmonicity is taken into account, with $1 \leftarrow 0$ transition being the strongest at the harmonic level while the anharmonic $3 \leftarrow 0$ transition being the strongest one. That change in the relative intensities is also observed in the RR spectrum of O_2 , showing the importance of using anharmonic wavefunctions when evaluating the RR spectrum.



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Table 1: Convergence of RR differential cross sections of $\nu_f \leftarrow \nu_i$ transitions in H_2 molecule with respect to the number of intermediate vibrational states. These cross sections include Herzberg-Teller and thermal (T=300K) corrections.

N_{ν_r}	$1 \leftarrow 0$		$2 \leftarrow 0$		$3 \leftarrow 0$	
	Harm.	Anharm.	Harm.	Anharm.	Harm.	Anharm.
2	$8.3 \cdot 10^{-28}$	$2.6 \cdot 10^{-28}$	$9.6 \cdot 10^{-28}$	$4.8 \cdot 10^{-28}$	$8.7 \cdot 10^{-28}$	$3.9 \cdot 10^{-28}$
14	$1.2 \cdot 10^{-27}$	$5.7 \cdot 10^{-29}$	$1.1 \cdot 10^{-27}$	$3.7 \cdot 10^{-28}$	$8.8 \cdot 10^{-28}$	$4.6 \cdot 10^{-28}$
26	$1.2 \cdot 10^{-27}$	$6.6 \cdot 10^{-29}$	$1.1 \cdot 10^{-27}$	$3.6 \cdot 10^{-28}$	$8.8 \cdot 10^{-28}$	$4.5 \cdot 10^{-28}$
38	$1.2 \cdot 10^{-27}$	$6.7 \cdot 10^{-29}$	$1.1 \cdot 10^{-27}$	$3.6 \cdot 10^{-28}$	$8.8 \cdot 10^{-28}$	$4.5 \cdot 10^{-28}$
54	$1.2 \cdot 10^{-27}$	$6.7 \cdot 10^{-29}$	$1.1 \cdot 10^{-27}$	$3.6 \cdot 10^{-28}$	$8.8 \cdot 10^{-28}$	$4.5 \cdot 10^{-28}$

Key-words: Vibronic Raman Spectroscopy; *Ab initio* methods; Anharmonicity.

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