Theor Chem Acc (2012) 131:1282
DOI 10.1007/s00214-012-1282-z

REGULAR ARTICLE

On the spectral intensities of vibrational transitions in polyatomic molecules: role of electrical and mechanical anharmonicities

Subrata Banik · M. Durga Prasad

Received: 20 May 2012 / Accepted: 16 September 2012
© Springer-Verlag Berlin Heidelberg 2012

Abstract A convergence study of intensities of transitions from vibrational ground state to the lower lying states is done with respect to the rank of the dipole moment surface (DMS) in the Taylor series expansion of the DMS. The relative roles of the mechanical and electrical anharmonicity are analyzed in the calculation of the intensities of vibrational transitions from ground state. We find that at least a quadratic expansion of the dipole moment functional is necessary to predict the intensities of vibrational transitions. The mechanical anharmonicity becomes important when the resonances between the vibrational states are significant.

Keywords Molecular vibrations · Vibrational coupled cluster · Spectral intensities

1 Introduction

The standard way to study the vibrational spectra of polyatomic molecules is the harmonic oscillator model. Here, the potential energy of the vibrational Hamiltonian is approximated at the second order in the Taylor series expansion of the potential energy function in the mass-weighted normal coordinates. The vibrational Hamiltonian for polyatomic molecules within this approximation is given by

$$H^{\mathrm{HO}} = \frac{1}{2}\sum_{i=1}^{3N-6}\left(-\frac{d^2}{dQ_i^2} + \omega_i^2 Q_i^2\right), \tag{1}$$

S. Banik · M. Durga Prasad (✉)
School of Chemistry, University of Hyderabad,
Hyderabad 500046, India
e-mail: mdpsc@uohyd.ernet.in

where ω_i is the harmonic frequency of ith mode. The vibrational wave functions in this case are just the product of $3N-6$ harmonic oscillator wave functions. The integrated band strength of a vibrational transition at zero temperature is

$$A(v_i) = 2.509.v_i.|\langle\Phi_F|D^{\alpha}(Q)|\Phi_I\rangle|^2 \quad \text{km/mol}, \tag{2}$$

where Φ_I and Φ_F are the initial and the final states between which the transition occurs, $D^{\alpha}(Q)$ are the dipole moment functions, and v_i is the reciprocal wave length of the transition energy. The standard way to calculate the dipole transition matrix elements is to use linear approximation in the Taylor series expansion of $D^{\alpha}(Q)$

$$D^{\alpha}(Q) = d_e^{\alpha} + \sum_i d_i^{\alpha} Q_i. \tag{3}$$

Here, α represents the x, y, and z directions; d_e^{α} is the equilibrium dipole moment; and the expansion coefficients $d_i^{\alpha} = \partial D^{\alpha}/\partial Q_i$ are the first derivatives of the electric dipole moment of molecule with respect to each normal coordinate. The harmonic oscillator model for the potential energy surface (PES) with the linear approximation in the dipole operator is termed as double harmonic approximation. Within the framework of this approximations, the selection rules for the allowed transitions are $\Delta v = \pm 1$ and $d_i^{\alpha} \neq 0$. Thus, in such a case, only the fundamental excitations are allowed from ground vibrational state.

Though such a double harmonic model provides reasonable description of molecular vibrational spectra, it is sometimes inadequate to account for the accurate experimental data. The overtone and combination bands are often prominent in the infrared spectra of molecules. There are two types of anharmonicity that affects the vibrational spectra. One is the mechanical anharmonicity that arises from the anharmonicity in the PES. The higher-order

Published online: 26 October 2012

potential energy terms in the Taylor series expansion are necessary to account for this mechanical anharmonicity. The potential energy in such case takes the form,

$$V(Q) = \frac{1}{2}\sum_i \omega_i^2 Q_i^2 + \sum_{i\le j\le k} f_{ijk} Q_i Q_j Q_k + \sum_{i\le j\le k\le l} f_{ijkl} Q_i Q_j Q_k Q_l + \cdots, \quad (4)$$

in mass-weighted normal coordinates. Here, the expansion coefficients $f_{ijk}, f_{ijkl,}$ etc, are the third, fourth, and so on derivatives of electronic energy with respect to the normal coordinates Q. The second source of anharmonicity comes from the higher-order terms in the dipole moment function

$$D^\alpha(Q) = d_e^\alpha + \sum_i d_i^\alpha Q_i + \sum_{i,j} d_{ij}^\alpha Q_i Q_j + \sum_{i,j,k} d_{ijk}^\alpha Q_i Q_j Q_k + \cdots \quad (5)$$

Here, d_{ij}^α, d_{ijk}^α, etc, are the second-, third-, and higher-order derivatives of the dipole moment vector with respect to the normal coordinates Q.

The intensity of a vibrational transition is a result of the interplay between mechanical and electrical anharmonicity. When an anharmonic PES and a linear dipole moment surface (DMS) are used, the spectral intensity of a multiple quantum transition is due to mechanical anharmonicity alone. Similarly, harmonic PES along with a nonlinear DMS leads to band strengths solely due to electrical anharmonicity. Several years ago, the relative roles of these two anharmonic effects in the spectral intestines were analyzed by Lenhmann and Smith [1] using one-dimensional model potentials representing the CH stretch of HCN molecule. They found that the mechanical anharmonicity is very significant for the spectral intensities of the transitions to high energy overtones of CH stretching mode. However, such a one-dimensional anharmonic potential does not account for the mechanical anharmonicity due to resonance interactions between different vibrational modes (e.g., Fermi resonance etc). This aspect was further discussed by McCoy and Sibert [2] in the context of the IR spectra of HCN and H_2CO. These authors stressed the role of mechanical anharmonicity due to intermode resonance coupling between different vibrational modes. Such type of resonances between different vibrational modes are stronger in H_2CO, and consequently, this type of mechanical anharmonicity plays more significant roles in the spectral intensities of H_2CO. For example, the $3_1 6_1$ and $2_1 6_1$ states borrow significant intensity from the near resonant 5_1 state due to mechanical anharmonicity. Recently, McCoy et al. [3] analyzed the role of mechanical and electrical anharmonicity on spectral intensities of a class of hydronium ion containing clusters.

Thus, the studies mentioned above underline the importance of including anharmonic terms in the PES and DMS for obtaining accurate band strengths. It is often found that a quartic truncation to the PES is adequate for the description of the lower lying vibrational states of molecules, if a high level of ab initio method is used with a large basis in the electronic structure calculations. The transition energies from such PES are comparable with experimental findings [4]. Algorithm to generate such quartic PES has been developed over the past few years [5, 6] and are now routinely available in standard quantum chemistry packages such as Gaussian 09 and GAMESS. However, the level of approximation to the DMS that gives the intensity values comparable to the experimental results is still unclear. Hu and coworkers [7] noted that intensity of vibrational transitions is very sensitive to the rank of the dipole surface. However, no systematic study on the level of approximation to the DMS that can lead to accurate intensities has been made to the best of our knowledge. The goal of the present work is to compare the intensities of transitions from vibrational ground state to lower lying excited states at different levels of approximation to the DMS to understand the convergence properties of Taylor series to the dipole operator. In other words, we ask the question "At what level should the dipole operator be truncated to give an acceptable spectrum ?" To answer this question, we calculate the band strengths of several transitions of water and formaldehyde. We truncate the dipole operator at different levels to understand the effect of higher-order terms on the overall band strength. The methodology used for calculating intensities is presented in Sect. 2, and the results are presented in Sect. 3. The Sect. 4 summarizes our conclusions.

2 Computational details

The vibrational Hamiltonian with harmonic potential in Eq. 1 is additively separable and the associated Schrödinger equation is exactly solvable. The vibrational wave function of a polyatomic molecule with N modes just a product of N harmonic oscillator wave functions

$$\Phi_I = \prod_\alpha \phi_{I_\alpha}^\alpha. \quad (6)$$

However, when the mechanical anharmonicity is present, the corresponding vibrational Hamiltonian is a many body Hamiltonian and hence an analytical solution is not possible. The Hamiltonian with a quartic truncation in the PES is given by

$$H = H^{\mathrm{HO}} + \sum_{i \le j \le k} f_{ijk} Q_i Q_j Q_k + \sum_{i \le j \le k \le l} f_{ijkl} Q_i Q_j Q_k Q_l. \tag{7}$$

Several ab initio methods have been developed to solve the Schrödinger equation associated with such Hamiltonian [8–29]. We use the vibrational coupled cluster method (VCCM) [24–29] in bosonic representation for our calculations. Specifically, we used the variant based on a double similarity transformation of the Hamiltonian. The ground state wave function in this variant of VCCM is parametrized as

$$|\psi_g\rangle = e^S e^{-\sigma} |\Phi_0\rangle \tag{8}$$

The VCCM with this ansatz was shown to give accurate excitation energies [24, 26] and transition matrix elements comparable to converged full vibrational configuration interaction (VCI) results [25, 27] with much less computational effort. The cluster operators S (σ) consist of connected singles, doubles, triples, and so on; excitation (de excitation) operators and Φ_0 are the optimized reference function for the ground state. It is parametrized as a multi-dimensional Gaussian [24],

$$\Phi_0 = N \exp[-\omega_i (Q_i - Q_i^0)^2/2], \tag{9}$$

and is optimized with respect to ω_i and Q_i^0.

The cluster operators are expanded as

$$S = \sum_i s_i a_i^\dagger + \sum_{i \le j} s_{ij} a_i^\dagger a_j^\dagger + \sum_{i \le j \le k} s_{ijk} a_i^\dagger a_j^\dagger a_k^\dagger + \cdots \tag{10}$$

$$\sigma = \sum_i \sigma_i a_i + \sum_{i \le j} \sigma_{ij} a_i a_j + \sum_{i \le j \le k} \sigma_{ijk} a_i a_j a_k + \cdots \tag{11}$$

Here, a and $a^\dagger$ are the harmonic oscillator ladder operators, and the reference function Φ_0 satisfies the relation

$$a_i |\Phi_0\rangle = 0. \tag{12}$$

The cluster matrix elements and the ground state energy are given by

$$\langle \Phi_I | H_{\mathrm{eff}} | \Phi_0 \rangle = 0. \tag{13}$$

$$\langle \Phi_0 | H_{\mathrm{eff}} | \Phi_I \rangle = 0. \tag{14}$$

$$\langle \Phi_0 | H_{\mathrm{eff}} | \Phi_0 \rangle = E_g. \tag{15}$$

Here, Φ_I are the excited states, and the effective Hamiltonian H_{eff} is

$$H_{\mathrm{eff}} = e^\sigma e^{-S} H e^S e^{-\sigma}. \tag{16}$$

The excited state wave functions are written as [24–27, 30]

$$|\psi_k\rangle = e^S \Omega_k |\Phi_0\rangle \tag{17}$$

Here, Ω_k is a linear excitation operator given by

$$\Omega_k = \sum_i \Omega_i^k a_i^\dagger + \sum_{i \le j} \Omega_{ij}^k a_i^\dagger a_j^\dagger + \sum_{i \le j \le k} \Omega_{ijk}^k a_i^\dagger a_j^\dagger a_k^\dagger + \cdots \tag{18}$$

The working equation for the excitation energies are given by the equation of motion,

$$[H_{\mathrm{eff}}, \Omega_k] |\Phi_0\rangle = \Delta E_k |\Phi_0\rangle. \tag{19}$$

Equation 19 is a vibrational CI-like equation, where H_{eff} is diagonalized in the configuration space defined by Ω_k operator. The eigenvalues of H_{eff} matrix are the vibrational excitation energies.

The working equations for the square of dipole transition matrix elements between two states $|\psi_i\rangle$ and $|\psi_j\rangle$ are given by [30]

$$|\langle \psi_i | D^\alpha | \psi_j \rangle|^2 = \langle L_i | D^\alpha_{\mathrm{eff}} | R_j \rangle \langle L_j | D^\alpha_{\mathrm{eff}} | R_i \rangle, \tag{20}$$

where, L_i and R_i are the left and right eigenvectors of H_{eff}, and,

$$D^\alpha_{\mathrm{eff}} = e^\sigma e^{-S} D^\alpha e^S e^{-\sigma}. \tag{21}$$

The results presented in the present work were obtained by the same program that was used to generate the results in Ref. [27].

3 Results and discussions

We calculated the transition energies and the associated band strengths of two molecules, water and formaldehyde. The PES and DMS were taken from the work of Handy and coworkers [31, 32]. These authors presented several quartic PES and cubic DMS for these two molecules. Among these, the set of surfaces generated by an MP2 calculation with a 6–31 Gext basis, as defined in Ref. [32] was judged to be the best. We used this set in our calculations.

The vibrational state calculations were carried out by truncating the cluster operators S and σ and the excitation operator Ω at six boson level. The results are presented below. Note that the vibrational modes are indexed according to the Mulliken convention.

We denote a linear dipole surface as D_1, a quadratic dipole surface as D_2, and a cubic dipole surface as D_3. In this study, we compare the pure mechanical intensity values (using the notation H/D_1), pure electrical intensity (H^{HO}/D_3) with H/D_3 numbers. We compare the results with H/D_2 and H/D_3 to analyze the importance of the rank of dipole operator in a particular transition. Only the transitions with band strength values greater than 0.1 km/mol are reported here.

Table 1 Transition energies and integrated band strength of vibrational transitions of H_2O at different rank of dipole function

State	Symmetry	Transition energy (cm^{-1})		Intensity (km/mol)					
		ν_{VCCM}	ν^{a}_{exp}	H/D_1	H/D_2	H/D_3	H^{HO}/D_1	H^{HO}/D_2	H^{HO}/D_3
2_1	a_1	1,561	1,595	63.84	64.09	66.24	64.18	64.18	66.19
2_2	a_1	3,090	3,152	0.25	0.13	0.15	0.00	0.75	0.75
1_1	a_1	3,678	3,657	4.61	4.92	4.91	4.60	4.60	4.60
3_1	b_1	3,788	3,756	58.48	58.23	60.23	59.87	59.87	61.79
1_12_1	a_1	5,192	5,235	0.03	0.17	0.22	0.00	0.05	0.05
2_13_1	b_1	5,274	5,331	0.17	1.41	1.35	0.00	0.59	0.59
1_13_1	b_1	7,420	7,250	1.41	0.80	0.85	0.00	0.03	0.03
3_2	a_1	7,552	7,445	0.02	0.30	0.30	0.00	0.16	0.16

[a] Reference [33]

The transition energies and the associated band strengths of water molecule are presented in Table 1. We note that the double harmonic model gives reasonably accurate results for the intensities of the fundamental transitions. The changes in the band strengths from the double harmonic value due to all the anharmonic contributions are less than about 5 % in all these transitions. The 1_1 band shows the maximum difference. The double harmonic intensity is hardly affected by the pure electrical anharmonicity. Nor does the pure mechanical anharmonicity affects the intensity to any significant extent. However, in the presence of both, the intensity changes by about 0.3 km/mol.

As mentioned in the introduction, the spectral intensity of an allowed transition depends on the strength of the mechanical and electrical anharmonicity and their relative phase. If the effects of the two terms are in phase (i.e., of the same sign), the overall change in the band strength would be more than the sum of the individual contributions. The 2_1 fundamental is an example of this type, though the magnitude of such enhancement is not very large.

Moving onto the two quantum transitions, we find that the interplay between electrical and mechanical anharmonicities is much more common and significant. Of the five two quantum transitions that have a band strength greater than 0.1, three show constructive interference between mechanical and electrical anharmonic effects. The 2_13_1 transition is a typical example. It is forbidden in the double harmonic approximation. It shows a band strength of 0.59 km/mol by pure electrical anharmonicity (H^{HO}/D_3), and 0.17 km/mol by pure mechanical anharmonicity (H/D_1). The total band strength is 1.35 km/mol, larger than the largest component by more than a factor of two. The remaining two transitions show destructive interference between electrical and mechanical anharmonic effects. For example, the band strength of the $1_13_!$ transition by pure electrical and pure mechanical anharmonicities is 0.03 and 1.41 km/mol, respectively. The net band strength is only 0.85 km/mol.

The variation of the band strength as one goes from H/D_1 to H/D_3 is quite small for the fundamental transitions, less than 5 %. It is much more significant for the two quantum states, For most of the states, however, the band strengths appear to be near convergence by H/D_3. For example, the band strength of 2_2 transition decreases from 0.25 to 0.15 km/mol as one goes from H/D_1 to H/D_3. The H/D_2 value is 0.13 km/mol.

The second example that we studied is formaldehyde. It has six vibrational modes. The transition energies and band strengths are presented in Table 2. The PES and the spectrum of formaldehyde are dominated by two Fermi resonances between mode 5 and modes 2 and 6, and modes 3 and 6. As a consequence, mechanical anharmonicities dominate some of the transitions to a much greater extent than seen in water.

Unlike water, double harmonic values of band strengths are nearly equal to the anharmonic values of only three fundamentals. Mode 2 has a large linear dipole term, $\delta D/\delta Q_2 = 0.174$, while $\delta D/\delta Q_3 = 0.07$. While the 2_1 and 3_1 states mix little, the large dipole component of the second mode allows 2_1 state to steal intensity to a large extent from the 3_1 state. A corresponding loss of intensity is seen from the 3_1 transition. As a result, these two fundamentals show a large deviation from the double harmonic value. The 5_1 transition is the other fundamental which has lost a major chunk of its intensity to the two states 3_16_1 and 2_16_1. This is due to Fermi resonance between these two states and the 5_1 state. The resulting large-scale mixing of 5_1 state with 2_16_1 and 3_16_1 states is the reason for this intensity redistribution rather than the large difference in the dipole derivatives as in the case of 2_1 and 3_1 states which mix to a limited extent.

The changes in the intensities of two quantum states from the double harmonic values follow the pattern observed in the case of water. For example, the band strength of 4_2

Table 2 Transition energies and integrated band strength of vibrational transitions of H_2CO at different rank of dipole function

State	Symmetry	Transition energy (cm^{-1})		Intensity (km/mol)					
		ν_{VCCM}	ν^{a}_{exp}	H/D_1	H/D_2	H/D_3	H^{HO}/D_1	H^{HO}/D_2	H^{HO}/D_3
4_1	b_1	1,157	1,167	6.92	6.97	6.51	6.93	6.93	6.43
6_1	b_2	1,239	1,249	9.97	10.06	10.76	9.68	9.68	10.25
3_1	a_1	1,505	1,500	6.75	6.38	6.74	9.22	9.22	9.69
2_1	a_1	1,719	1,746	69.73	67.40	70.89	66.47	66.47	67.43
4_2	a_1	2,308	2,327	1.04	0.30	0.33	0.00	2.35	2.35
6_2	a_1	2,476	2,500	0.89	0.25	0.25	0.00	0.26	0.26
3_16_1	b_2	2,707	2,719	19.80	17.00	17.83	0.00	0.23	0.23
1_1	a_1	2,830	2,782	65.57	74.34	72.90	70.95	70.95	69.93
2_14_1	b_1	2,867	2,905	0.00	0.15	0.15	0.00	0.17	0.17
5_1	b_2	2,870	2,843	51.31	57.00	59.89	101.60	101.60	106.65
2_16_1	b_2	2,989	3,000	27.51	29.82	30.85	0.00	0.00	0.00
3_2	a_1	3,008	3,000	0.21	1.85	1.85	0.00	0.71	0.71
2_2	a_1	3,420	3,472	0.70	5.36	5.72	0.00	2.13	2.13
1_16_1	b_2	4044	–	0.00	0.10	0.12	0.00	0.05	0.05
2_15_1	b_2	4,552	–	0.05	0.40	0.39	0.00	1.73	1.73
5_2	a_1	5,718	5,651	0.15	0.08	0.72	0.00	4.78	4.78

[a] Reference [34]

transition is due to a destructive interference between electrical and mechanical anharmonicities, while 2_2 transitions is very intense due to constructive interference.

As in the case of water, here also, the band strengths are almost converged by H/D_3 except in the 5_2 transition.

4 Conclusion

We made a systematic study of the effect of truncation of the rank of the dipole operator on the calculated intensities of the vibrational transitions from ground state to lower lying excited states. With the illustrative example of water and formaldehyde molecules we studied, we find that the double harmonic approximation does not provide reasonable accuracy in the spectral intensities of the fundamental states in all cases. For the other low energy states with multiple quanta excitations, where the coupling between the vibrational levels is small, the electrical anharmonicity plays more important role in the spectral transition. However, for the states where the Fermi resonance is strong, the mechanical anharmonicity dominates. From the convergence pattern of the spectral intensities with respect to the rank of the dipole operator, we find that the intensity values are saturated with a quadratic DMS for transitions to two quanta states. Thus, a quadratic expansion in the DMS along with a quartic PES might be adequate for predicting intensities for two quanta transitions. However, for transitions to the higher quantum states, a cubic DMS is desirable to calculate the spectral intensity.

Acknowledgments SB acknowledges the Dr. D. S. Kothari postdoctoral fellowship from UGC, India. MDP acknowledges support from UGC, India, in the form of CAS to the School of Chemistry, UPE to the University of Hyderabad and DST, India, for HPCF facility at the University of Hyderabad.

References

1. Lenhmann KK, Smith AM (1990) J Chem Phys 93:6140
2. McCoy AB, Sibert EL (1991) J Chem Phys 95:3488
3. McCoy AB, Guasco TL, Leavitt CM, Olesen SG, Johnson MA (2012) Phys Chem Chem Phys 14:7205
4. Aoyagi M, Gray SK (1991) J Chem Phys 94:195
5. Barone V (2004) J Chem Phys 120:3059
6. Hansen MB, Christiansen O, Toffoli D, Kongsted J (2008) J Chem Phys 128:174106
7. Liu A, Hu S, Zhu Q (2005) J Chem Phys 123:174305
8. Carney DC, Sprandel LL, Kern CW (1978) Adv Chem Phys 37:305
9. Bowman JM (1978) J Chem Phys 68:608
10. Bowman JM (1986) J Chem Phys 19:202
11. Christoffel KM, Bowman JM (1982) Chem Phys Lett 85:220
12. Carter S, Handy NC (1986) Comput Phys Rep 5:117
13. Carter S, Meyer W (1990) J Chem Phys 93:8902
14. Culot F, Liévin J (1994) Theor Chim Acta 89:227
15. Culot F, Laruelle F, Liévin J (1995) Theor Chim Acta 92:221
16. Heislbetz S, Rauhut G (2010) J Chem Phys 132:124102
17. Jung JO, Gerber RB (1996) J Chem Phys 105:10332
18. Chaban G, Jung JO, Gerber RB (1999) J Chem Phys 111:1823
19. Matsunaga N, Chaban GM, Gerber RB (2002) J Chem Phys 117:3541
20. Yagi K, Hirata S, Hirao K (2008) Phys Chem Chem Phys 10:1781
21. Sibert EL (1988) J Chem Phys 88:4378
22. McCoy AB, Sibert EL (1990) J Chem Phys 92:1893
23. McCoy AB, Sibert EL (1991) J Chem Phys 95:3476

24. Nagalakshmi V, Lakshminarayana V, Sumithra G, Durga Prasad M (1994) Chem Phys Lett 217:279
25. Durga Prasad M (2000) Indian J Chem 39:196
26. Banik S, Pal S, Durga Prasad M (2008) J Chem Phys 129:134111
27. Banik S, Pal S, Durga Prasad M (2010) J Chem Theor Comput 6:3198
28. Christiansen O (2004) J Chem Phys 120:2149
29. Seidler P, Christiansen O (2009) J Chem Phys 131:234109
30. Durga Prasad M (1994) Theor Chim Acta 88:283
31. Green WH, Willetts A, Jayatilaka D, Handy NC (1990) Chem Phys Lett 169:127
32. Willets A, Handy NC, Green WH, Jayatilaka D (1990) J Phys Chem 94:5608
33. Rothman LS, Gamache RR, Goldman A, Brown LR, Toth RA, Picket HM, Poynter RL, Flaud JM, Camy-Peyret C, Barbe N, Husson N, Rinsland CP, Smith MAH (1987) Appl Optics 26:1045
34. Reisner RA, Field RW, Kinsey JL, Dai HL (1984) J Chem Phys 80:5968