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Quantum Groups and Spectra of Diatomic Molecules [1]

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Abstract

We briefly review and further investigate the quantum group approach to the spectra of the diatomic molecules presented by the authors recently. The vibration-rotational structures as well as the interactions of vibrations and rotations are described in the quantum group theoretic approach satisfactorily. When Taylor expanded, the analytic formulae of the new approach reproduce the results of nonlinear vibrating rotator model. For some particular states of randomly selected molecules, the parameters of the new approach are computed to fit the phenomenological data to high accuracies.

We also supply an analysis of the (pseudo-) potential implied in the new model, and compare it with the conventional model of the local potential that are applied in the explanation of the Dunham formula of energy spectra.

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I. Introduction

As is well known, most of the progresses in modern physics are accompanied with the studies of symmetries. Quitely recently, much attentions have been directed to the investigations on the quantum groups [1][2][3][4][5][6] and Yang-Baxter equations [7][8] which are deeply rooted in many physical theories [4][9]. The quantum groups (in Jimbo's proposal [2][4]) are single parameter deformations of Lie algebras, which are convenient to be studied in the framework of Hopf algebra and non-commutative geometry [3][10].

It is a widely accepted opinion that when the deformation parameter q is not a root of unity, it is a function of Planck constant $\hbar$, *e.g.*, $\ln q \propto \hbar$. When $\hbar \rightarrow 0$, $q \rightarrow 1$ and the quantum group symmetries reduce to Lie group symmetries, while the quantum systems revert to classical ones. As we pointed out [13][14][15][16], this is not evident. In fact, the q-deformation and canonical quantization can be two independent concepts. It is possible to find the q-deformed symmetries (with nontrivial Hopf algebra structure [16]) in classical systems, and when the systems are canonically quantized, one obtains quantum group symmetries in quantum systems. The quantum systems described by quantum symmetries reduce to the quantum systems possess ordinary Lie symmetries when the deformation parameter q equals one.

This viewpoint brings new possibilities to the studies of quantum groups as potential dynamical symmetries of physical systems. As the quantum groups, with respect to their Lie counterparts, introduce independent parameters q's, the new symmetries allow violations of the Lie symmetries. When q's are not unity, the new symmetries are exact symmetries in the point of view of Hopf algebras and with well established theory of representation and spectrum, but violations of the Lie symmetries occur. The violations are small if the deviations of q's from unity are small. If the deviations get greater, the violations get greater. The most well known model with the quantum group symmetry is the Heisenberg spin chain of XXZ type, where the difference of Z from X induces the violation of $SU(2)$ symmetry. But the violation therein does not break the symmetry of $SU_q(2)$, which is one of the best studied quantum groups.

In the attempts to find other systems in which the quantum groups are possible dynamical symmetries, the authors looked into the century old problem of the rotating and vibrating diatomic molecule. It is well known that at the lowest order approximation, the internal motion of the molecule is treated as two separated motions, *i.e.*, the linear vibration and rigid rotation obeying the Lie symmetries (algebras) $H(4)$ and $SU(2)$ respectively. But the deviations exist between the real motions in molecules and the simple descriptions: these two symmetries are violated. To fit the experimental data, phenomenological treatments are introduced, which can be explained by anharmonic oscillator and non-rigid rotator or other sophisticated models [20][21][22][23].

Although these treatments are effective and well studied, the authors deem it beneficial to find proper symmetries with analytic interpretations of the phenomenological resolutions of such systems, and the quantum group symmetries are suggested as satisfactory candidates to describe the violation of the Lie symmetries to certain order.

It is shown in this paper that the Dunham formula [19]

$$E_{vr}(v,J) = hc\sum_{ij} Y_{ij}\left(v+\frac{1}{2}\right)^i (J(J+1))^j, \tag{1}$$

for the vibration-rotational energy spectrum of the diatomic molecule, (with v and J being the quantum numbers of vibration and rotation, and Y_{ij} the Dunham coefficients) can be reproduced from the Taylor expansion of the quantum group theoretic formula. The specific character of this approach is that it does not go to the detail of the binding potential, but demonstrates that the energy levels and selection rules are appropriate for any diatomic molecular-like systems that possess the Dunham-like energy spectrum and are dominated by dipole degrees of freedom by using a spectrum generating algebra focusing on the elementary quantity involved in the interaction and not on the interaction potential.

Although the new approach does not need the explicit form of the binding potential, we supply an explicit analysis of the (pseudo-) potential implied in the new model, and compare it with the model of the conventional local potential applied in the explanation of the Dunham formula of energy spectra.

Under the adiabatic condition, the Schrödinger equation for a diatomic molecule is conventionally

$$\left[-\frac{h^2}{8\pi^2 m_1}\nabla_1^2 - \frac{h^2}{8\pi^2 m_2}\nabla_2^2 + V(r)\right]\Phi = E\Phi, \tag{2}$$

where m_1 and m_2 are masses for the nuclei, V is the effective potential between them. In the center of mass frame the equation reads

$$\left(-\frac{h^2}{8\pi^2 m}\nabla^2 + V(r)\right)\Psi(\vec{r}) = E\Psi(\vec{r}), \tag{3}$$

where $m = \dfrac{m_1 m_2}{m_1 + m_2}$ is the reduced mass. As the variables can be separated, we have

$$\Psi(\vec{r}) = R(r)Y_{JM}(\theta,\phi), \quad R(r) = \frac{1}{r}\psi(r), \tag{4}$$

where $Y_{JM}(\theta,\phi)$ are spheric harmonics. The tangent motion is rigid rotation described by $SU(2)$ algebra or isomorphically $SO(3)$ algebra while the radial motion satisfies the following equation,

$$\left\{-\frac{h^2}{8\pi^2 m}\frac{d^2}{dr^2}+\frac{J(J+1)h^2}{8\pi^2 mr^2}+V(r)\right\}\psi=E\psi. \tag{5}$$

Under the lowest order approximation, the effective moment of inertia can be treated as a constant. If one makes a further approximation of $V(r)\propto r^2$, then (3) becomes the motion equation for rigid rotation and another separate motion of linear vibrating (*i.e.*, the dumbell and linear oscillator model), with the eigenvalues of Hamiltonian easily given in the following

$$E_{vr}=hc\omega_e(v+\frac{1}{2})+hcB_eJ(J+1), \tag{6}$$

with the Hamiltonian

$$H_{vr}=hc\omega_e\left(N+\frac{1}{2}\right)+hcB_eC \tag{7}$$

where C is the Casimir operator of the $SU(2)$ algebra, and

$$N=-\frac{h}{8\pi^2 mc\omega_e}\frac{\partial^2}{\partial x^2}+\frac{2\pi^2 mc\omega_e}{h}x^2-\frac{1}{2} \tag{8}$$

is the particle number operator of the linear oscillator, where $x=r-r_e$ is the change of the internuclear distance from equilibrium position. In obtaining this simple model one ignores the terms involving the quantum number of rotations, J. So it does not provide the description of the vibration-rotational structures of diatomic molecules.

In fact, the observed spectra deviate qualitatively from that given by the above model. In vibrational spectrum, the separations between the adjacent lines are not exactly equidistant, but becoming narrower toward the shorter or longer wavelength. To fit the experimental results better, one has to consider the nonlinear modifications to the simple harmonic oscillator model, which should be in the following form,

$$E_{vib}=hc\omega_e\left(v+\frac{1}{2}\right)-hc\omega_e x_e\left(v+\frac{1}{2}\right)^2+hc\omega_e y_e\left(v+\frac{1}{2}\right)^3+\cdots, \tag{9}$$

which is (a special case of) Dunham formula (1)[19].

In rotational spectrum, the separations of the adjacent rotational energy levels are not exactly that of dumbbell model, either. Small but important deviations arise. To meet the experimental results, one has to consider nonlinear modifications to the dumbbell model. That is the Dunham formula with vanishing vibrational excitation in the following form,

$$E_{rot} = hcB_eJ(J+1) - hcD_eJ^2(J+1)^2 + \cdots. \tag{10}$$

The most direct conjecture of the Hamiltonian should be as follows

$$H_{rot} = hcB_eC - hcD_eC^2 + \cdots, \tag{11}$$

where C is the Casimir operator of Lie algebra $SU(2)$. Of course, one can also interpret the above Hamiltonian ad a description of the vibrator with moment of inertia dependent on the rotational excitations, such that the expansion of the latter coincides with the newly proposed one [21][23][22]. But as we shown in [25][26]citemolecule4 and the following, an apparently alternative interpretation is that the power series in $J(J+1)$ is an expansion of a more compact formula in the quantum group theoretic approach.

Fine structure of spectra of the vibrating and rotating diatomic molecules shows interactions between vibrations and rotations, *i.e.*, a simultaneous rotation and vibration occurs. For this reason, a model in which simultaneous rotation and vibration takes place, the vibrating rotator model should be considered. In the picture of the model of vibrating rotator, the rotational constants B_e, D_e, $\cdots$ in (10) should be replaced by the vibration-rotational constants B_v, D_v, $\cdots$. To a first order (usually satisfactory) approximation, the set of vibration-rotational constants can be expressed as

$$\begin{aligned} B_v &= B_e - \alpha_e(v + \frac{1}{2}) + \cdots \\ D_v &= D_e + \beta_e(v + \frac{1}{2}) + \cdots \end{aligned} \tag{12}$$

where α_e and β_e are constants which are small compared to B_e and D_e respectively.

We obtain, accordingly, for the rotational energy levels in a given vibrational level

$$E_{rot}(J) = hcB_vJ(J+1) - hcD_vJ^2(J+1)^2 + \cdots. \tag{13}$$

By taking into account of vibration and rotation in this way, we obtain for the energy levels of a vibrating rotator

$$\begin{aligned} E_{vr}(v,J) &= E_{vib} + E_{rot} \\ &= hc\omega_e\left(v+\tfrac{1}{2}\right) - hc\omega_ex_e\left(v+\tfrac{1}{2}\right)^2 + hc\omega_ey_e\left(v+\tfrac{1}{2}\right)^3 + \cdots \\ &\quad + hcB_eJ(J+1) - hcD_eJ^2(J+1)^2 + \cdots, \end{aligned} \tag{14}$$

or written into the following form

$$\begin{aligned} E_{vr}(v,J) &= hc\omega_e\left(v+\tfrac{1}{2}\right) - hc\omega_e x_e\left(v+\tfrac{1}{2}\right)^2 + hc\omega_e y_c\left(v+\tfrac{1}{2}\right)^3 \\ &\quad -hc\alpha_e(v+\tfrac{1}{2})J(J+1) - hc\beta_e(v+\tfrac{1}{2})(J(J+1))^2 \\ &\quad +hcB_eJ(J+1) - hcD_eJ^2(J+1)^2 + \cdots . \end{aligned} \tag{15}$$

The thorough phenomenological description of vibrational and rotational structure of diatomic molecules is given by Dunham formula, see (1) and [19]. A successful theoretic approach with quantum group symmetry $H_q(4) \otimes SU_{q'}(2)$ must recover the important leading terms of Dunham formula. Because of the interaction between the rotation and vibration in the molecule, it is reasonable to consider that the deformation parameter of $H_q(4)$ may depend on the eigenvalue of the Casimir operator of $SU_{q'}(2)$, and *vica versa*.

As we addressed in the above about the constructions of the vibrational and rotational Hamiltonians, the direct construction of the vibration-rotational system should be

$$H_{vr}(v,J) = hc\sum_{ij} Y_{ij}\left(N+\frac{1}{2}\right)^i (C)^j , \tag{16}$$

which is an expansion in the generators of the Heisenberg and $SU(2)$ algebras.

In the previous publications [24][25][26][27], we proposed the quantum group theoretic model possess the quantum group symmetries $H_q(4)$ and $SU_q(2)$. These quantum group generators can be expressed in terms of the Lie counterparts. In this approach, we actually did things in the inverse way: The Dunham formulas (1,10,1) or the Hamiltonians (94,11,16) were compactified into quantum group generators. We derived the coefficient constants, ω_e, $\omega_e x_e$, $\omega_e y_e$, B_e, D_e and α_e, β_e, appear in the formula (15), *i.e.*, Y_{10}, Y_{20}, Y_{30}, Y_{01}, Y_{02} and Y_{11}, Y_{21} in the Dunham formula (1), from the theoretic approach of quantum group theory [24][25][26][27].

Section II is devoted to the proposal of the $H_q(4)$ symmetry to explain the pure vibrational spectra, the $SU_q(2)$ algebra for the pure rotational spectra is reviewed in section III, and in section IV, the hybrid symmetry $H_{q(J)}(4) \otimes SU(2)$ is reviewed as a thorough description of the vibration-rotational spectra with the dependence of q on the rotational excitation J characterizes the interaction between the rotation and vibration. Section V presents some short discussions and remarks.

II. $H_q(4)$ Quantum Group Symmetry and the Vibrational Spectrum

The Hamiltonian for q-oscillator system is [11][12][13][14][15][16][28]

$$H_{q-vib} = \frac{1}{2}\left(a_q^\dagger a_q + a_q a_q^\dagger\right) hc\nu_{vib} \tag{17}$$

where a_q, $a_q^\dagger$ are annihilation and creation operators for the deformed oscillator. These operators are connected with the operators $a, a^\dagger$ of the simple harmonic oscillator in the following way

$$a_q = \sqrt{\frac{[N+1+b\gamma]_q}{N+1}}\,a, \qquad a_q^\dagger = a^\dagger\sqrt{\frac{[N+1+b\gamma]_q}{N+1}}. \tag{18}$$

where $N = a^\dagger a$, $[m]_q = \frac{q^m - q^{-m}}{q - q^{-1}}$, $\gamma = \ln q$ and b an arbitrary constant. From the basic commutation relations

$$[a, a^\dagger] = 1, \quad [a, a] = [a^\dagger, a^\dagger] = 0, \tag{19}$$

we have the commutation relations for the q-oscillator system

$$\begin{aligned} \left[a_q, a_q^\dagger\right] &= [N+1+b\gamma]_q - [N+b\gamma]_q\,, \\ [N, a_q] &= -a_q, \quad \left[N, a_q^\dagger\right] = a_q^\dagger. \end{aligned} \tag{20}$$

This is the q-deformed oscillator algebra $H_q(4)$. According to [22], the Hopf operations: coproduct, antipode and counit can be defined for this algebra. Because it is neither commutative nor co-commutative, $H_q(4)$ is a quantum group. The universal R-matrix to the Yang-Baxter equation can also be constructed. The Hamiltonian (17) can be written as

$$\begin{aligned} H_{q-vib} &= \tfrac{1}{2}\left([N+b\gamma]_q + [N+1+b\gamma]_q\right) hc\nu_{vib} \\ &= \frac{hc\nu_{vib}}{2\sinh(\gamma/2)}\sinh\left(\gamma\left(N+\frac{1}{2}+b\gamma\right)\right). \end{aligned} \tag{21}$$

The energy levels for this system are

$$\begin{aligned} E_{q-vib} &= \tfrac{1}{2}\left([v+1+b\gamma]_q + [v+b\gamma]_q\right) hc\nu_{vib}, \\ &= H\sinh\left(v+\tfrac{1}{2}+b\gamma\right) \end{aligned} \tag{22}$$

where $H = \dfrac{hc\nu_{vib}}{2\sinh(\gamma/2)}$.

We suppose the vibrational structure of diatomic molecules can be described by the q-oscillator model. Then vibrational energy levels of the diatomic molecules is of the form

$$\begin{aligned} E_{vib} &= E_0 + E_{q-vib} \\ & \quad E_0 + H\sinh\left(v+\tfrac{1}{2}+b\gamma\right) \end{aligned} \tag{23}$$

where E_0 are the energy levels of electrons. The above equation can be Taylor-expanded into

$$\begin{aligned} E_{vib} = \quad & hc\nu_{vib}\left\{\frac{\sinh(\gamma c)}{2\sinh(\gamma/2)} + \cosh(\gamma c)\left(v+\frac{1}{2}\right) + \frac{\gamma\sinh(\gamma c)}{2}\left(v+\frac{1}{2}\right)^2 + \right. \\ & \left. \frac{\gamma^2\cosh(\gamma c)}{6}\left(v+\frac{1}{2}\right)^3 + \cdots\right\} + E_0, \end{aligned} \tag{24}$$

where $c = b\gamma$. The leading terms coincide with (8) if the new parameters are properly chosen. The examples are given in table 2, where eighteen vibrational curves are refitted in table 1 by the quantum group symmetric model.

The representations of quantum group $H_q(4)$ can be constructed in the following way. The states are given by

$$|v>>= ([v+b\gamma]_q!)^{-1/2}\left(a_q^{\dagger}\right)^v |0> . \tag{25}$$

The actions of the operators on the Fock states yield

$$\begin{aligned} a_q^{\dagger}|v>> &= \sqrt{[v+1+b\gamma]_q}|v+1>>, \\ a_q|v>> &= \sqrt{[v+b\gamma]_q}|v-1>>, \\ a_q|0> &= 0. \end{aligned} \tag{26}$$

It is easy to see that the above representation for quantum group $H_q(4)$ is isomorphic to that for the ordinary harmonic oscillator algebra $H(4)$. [3]

$$\begin{aligned} |v>> &= ([v+b\gamma]_q!)^{-1/2}\left(a_q^{\dagger}\right)^v |0>, \\ &= (v!)^{-1/2}\left(a^{\dagger}\right)^v |0>, \\ &= |v> . \end{aligned} \tag{27}$$

where $|v>$ are the Fock states for the ordinary harmonic oscillator. Therefore the representation in coordinate space can be expressed exactly in Hermite polynomials,

$$\tilde{\psi}_v(x) = N_v H_v(X) e^{-X^2/2}. \tag{28}$$

where $X = \beta x$, x is the change of the internuclear distance from the equilibrium position, $\beta = \left((2\pi)^2 mc\nu_v/h\right)^{1/2}$ and $N_v = (\sqrt{\pi}2^v v!)^{-1/2}$.

If the molecule in its equilibrium position has a dipole moment, as is always the case for molecule consisting of unlike atoms, this dipole moment changes if the internuclear

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[3] For q a root of unity, the properties of the representation are more complicated, see [6][18][15][28].

distance changes. As a first order approximation, the dipole moment is assumed to vary linearly with the internuclear distance, *i.e.*, $M = M_0 + M_1 x$, where M_0 is the dipole moment in the equilibrium position, and M_1 the rate of change of the dipole moment with the internuclear distance. Therefore the transition matrix elements are

$$R_q^{v'v''} = \int \tilde{\psi}_{v'}^* M \tilde{\psi}_{v''} dx = M_0 \delta_{v'v''} + M_1 \frac{N_{v'} N_{v''}}{\beta} \int X H_{v'}(X) H_{v''}(X) e^{-X^2} dx. \quad (29)$$

By the recursion relation of the Hermite polynomial, the second term in the above equation vanishes unless $v' = v'' \pm 1$. Hence the selection rule for the q-oscillator is $\Delta v = \pm 1$. Therefore the infrared spectra of q-oscillator is

$$\nu = \frac{1}{2} \left([v + 2 + b\gamma]_q - [v + b\gamma]_q \right) \nu_{vib}. \quad (30)$$

A dipole moment $\vec{p}$ is induced in the diatomic system when it is brought into an external electric field. The magnitude of the resulting dipole moment is proportional to that of this field, *i.e.*,

$$|\vec{p}| = \alpha |\vec{F}|, \quad (31)$$

where α is called polarizability. The scattering matrix elements corresponding to the induced dipole moment are

$$|\vec{p}|^{v'v''} = \int \tilde{\Psi}_{v'}^* \vec{p} \tilde{\Psi}_{v''} dx, \quad (32)$$

where $\tilde{\Psi}_{v'}$ and $\tilde{\Psi}_{v''}$ are the time dependent wave functions for q-oscillator at states v' and v'' respectively. So there should be the evolution factors $e^{2\pi i (E_{v'}/\hbar)t}$, $e^{-2\pi i (E_{v''}/\hbar)t}$ and $e^{2\pi i c \nu_{ele} t}$ in the functions $\Psi_{v'}$, Ψ_v'' and $\vec{p}$. So $|\vec{p}|^{v'v''}$ varies in frequency $c\nu_{ele} + (E_{v'} - E_{v''})/h$ and amplitude

$$|\vec{p}|^{v'v''} = |\vec{F}| \int \tilde{\psi}_{v'}^* \alpha \tilde{\psi}_{v''} dx. \quad (33)$$

In a first order approximation, we may assume a linear variation of α with the displacement x from the equilibrium position,

$$\alpha = \alpha_{0v} + \alpha_v^1 x, \quad (34)$$

therefore we have

$$|\vec{p}|^{v'v''} = |\vec{F}| \alpha_{0v} \int \tilde{\psi}_{v'}^* \tilde{\psi}_{v''} dx + |\vec{F}| \alpha_v^1 \int x \tilde{\psi}_{v'}^* \tilde{\psi}_{v''} dx. \quad (35)$$

Because of the orthogonality of the wave functions of q-oscillator, the first term in the above equation is zero unless $v' = v''$, which gives the Reighley scattering. The integration in the second term vanishes unless $v' = v'' \pm 1$. So the selection rule for vibrational Raman spectrum is $\Delta v = \pm 1$. We obtain the vibrational Raman spectrum from the energy levels given in (18),

$$\nu = \nu' \pm \left(E'_{v+1} - E_v\right) = \nu' \pm \frac{1}{2}\left([v + 2 + b\gamma]_q - [v + b\gamma]_q\right) \nu_{vib}, \tag{36}$$

where ν' is the wave number of the incident light.

The transitions between electronic states are involved in the spectra of visible and ultraviolet regions. The vibrational spectrum of electronic transitions is

$$\nu = T' - T'' = (T'_e - T''_e) + (G' - G'') = \nu_e + \nu_v \tag{37}$$

where ν_e is a quantity depending on the transition between the electronic states. From (18) we rewrite (37) into

$$\begin{aligned} \nu = \nu_e + \tfrac{1}{2}\{\, & \nu'_{vib}\left([v' + 1 + b'\gamma']_{q'} + [v' + b'\gamma']_{q'}\right) \\ & -\nu''_{vib}\left([v'' + 1 + b''\gamma'']_{q''} + [v'' + b''\gamma'']_{q''}\right)\}. \end{aligned} \tag{38}$$

An investigation of the selection rules shows that for electronic transitions there is no strict selection rule for the vibrational quantum number v. In principle, each vibrational state of the upper electronic state can be combined with each vibrational state of lower electronic state, i.e., there is no restriction to the quantum numbers v' and v'' in (38), and therefore (38) gives very complicated spectral structures.

If the quantum number v' in (38) is fixed, then the v'' progression is formed. In the v'' progression the upper vibrational state is fixed while the lower vibrational state is different. Hence (38) is rewritten into

$$\nu = \nu''_0 - \frac{1}{2}\left([v'' + 1 + b''\gamma'']_{q''} + [v'' + b''\gamma'']_{q''}\right) \nu''_{vib}, \tag{39}$$

where the quantum number ν''_0 is ν_e plus the fixed vibrational spectrum in the upper electronic state, and therefore a constant.

If the quantum number v'' is chosen to be a constant, then the v' progression is formed in which different vibrational state in an upper electronic state combining with one vibrational state of lower electronic state. And it is therefore expressed in the following formula

$$\nu = \nu'_0 + \frac{1}{2}\left([v' + 1 + b'\gamma']_{q'} + [v' + b'\gamma']_{q'}\right) \nu'_{vib}, \tag{40}$$

where ν'_0 is ν_e minus the fixed vibrational spectrum of the lower electronic state, and therefore a constant.

We rewrite the formula for the infrared spectra of q-oscillator into

$$\nu = \nu_{vib}\sinh\gamma\left(v+\frac{1}{2}+c_1\right), \tag{41}$$

where $c_1 = \frac{i\pi}{2\gamma}+\frac{1}{2}+b_1\gamma$. Similarly, the formula for vibrational Raman spectra is written into the following form

$$\nu = \nu' \pm \nu_{vib}\sinh\gamma\left(v+\frac{1}{2}+c_1\right). \tag{42}$$

The v'' progression given in formula (39) can be rewritten as

$$\nu = \nu_0'' - \frac{\nu''_{vib}}{2\sinh\gamma''}\sinh\gamma''\left(v+\frac{1}{2}+c_2''\right), \tag{43}$$

where $c_2'' = b_2''\gamma''$. The v' progression (40) can be rewrite in the same way

$$\nu = \nu_0' + \frac{\nu'_{vib}}{2\sinh\gamma'}\sinh\gamma'\left(v+\frac{1}{2}+c_2'\right), \tag{44}$$

where $c_2' = b_2'\gamma'$.

III. $SU_q(2)$ Quantum Group Symmetry and the Rotational Spectrum

The q-rotator model [25][26], as an exactly solvable system, is the q-deformed rotator with the quantum group symmetry $SU_q(2)$. The Hamiltonian for this system is, namely

$$H_{q-\mathrm{rot}} = \hbar^2\frac{C_q}{2I}, \tag{45}$$

where C_q is the Casimir operator for the quantum group $SU_q(2)$. In terms of the generators of $SU_q(2)$, C_q can be written as

$$C_q = J_q^- J_q^+ + [J_q^3]_q[J_q^3+1]_q, \tag{46}$$

where $J_q^\pm$, J_q^3 are generators of $SU_q(2)$.

As is well known, quantum group $SU_q(2)$ is the q-deformation of Lie algebra $SU(2)$ with the following algebraic relations,

$$[J_q^+, J_q^-] = [2J_q^3]_q, \quad [J_q^3, J_q^\pm] = \pm J_q^\pm. \tag{47}$$

The Hopf operations, R-matrix and quantum Yang-Baxter equation can be constructed [7][8][1][4] [2][9]. It can be shown that this quantum group can be realized by $SU(2)$ generators in the following way [4],

$$\begin{aligned} J_q^+ &= \sqrt{\frac{[J^3+j]_q[J^3-1-j]_q}{(J^3+j)(J^3-1-j)}}J^+, \\ J_q^- &= J^-\sqrt{\frac{[J^3+j]_q[J^3-1-j]_q}{(J^3+j)(J^3-1-j)}}, \\ J_q^3 &= J^3, \end{aligned} \tag{48}$$

where j is an operator formally expressed as follows,

$$j = -\frac{1}{2} + \sinh^{-1}\left(\frac{\sinh\gamma}{\gamma}\sqrt{C_q + \left[\frac{1}{2}\right]_q^2}\right), \tag{49}$$

where $\gamma = \ln q$. C_q can be expanded into a series of C, which is the Casimir operator of the usual Lie group $SU(2)$. *i.e.*,

$$C_q = \left(1 - \frac{1}{6}\gamma^2 + \frac{7}{360}\gamma^4\right)C + \gamma^2\left(\frac{1}{3} - \frac{7}{90}\gamma^2\right)C^2 + \frac{2\gamma^4}{45}C^3 + o(\gamma^5), \tag{50}$$

which is similar to (17). The coincidence of the leading terms in the above equation and (17) hints us the possibility of some applications of quantum group in simple quantum systems.

When q is not the root of unity, it is easy to see that the representation of $SU_q(2)$ can be chosen to be that of $SU(2)$ (up to a phase factor)[5]. Therefore, representations of quantum group $SU_q(2)$ are completely reducible, and the irreducible ones can be classified according to the highest weights [5]. They can be chosen to be the spherical harmonics , *i.e.*,

$$\tilde{\Psi}_{JM}(\vec{x}) = Y_{JM}(\theta, \phi). \tag{51}$$

The action of the generators of $SU_q(2)$ yields

$$\begin{aligned} J_q^\pm\tilde{\Psi}_{JM}(\vec{x}) &= \sqrt{[J \mp M]_q[J \pm M + 1]_q}\,\tilde{\Psi}_{J,M\pm1}(\vec{x}), \\ J_q^3\tilde{\Psi}_{JM}(\vec{x}) &= M\tilde{\Psi}_{JM}(\vec{x}). \end{aligned} \tag{52}$$

While the action of the Casimir operator C_q yields

$$C_q\tilde{\Psi}(\vec{x}) = \frac{\hbar^2}{2I}[J]_q[J+1]_q\tilde{\Psi}(\vec{x}). \tag{53}$$

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[4] A phase factor can be added similarly to the case of q-oscillator, see [13][14][15][16].

[5] When q is the root of unity, odd things may appear, see [6][15][18][28].

Hence the eigenvalues of the Hamiltonian of the q-rotator system are

$$E_{q-\mathrm{rot}} = \frac{h^2}{8\pi^2 I}[J]_q[J+1]_q. \tag{54}$$

This model is a non-rigid rotator, and the deformation parameter γ is a variable to be chosen phenomenologically which characterizes the non-rigidity. When γ is zero, the above equation describes the rigid rotator with the constant moment of inertia I.

Now we are in the position to set up the q-rotator model for diatomic molecules. As is always the case for molecules consisting of unlike atoms, there is an internal dipole moment M_0 with spatial components,

$$\begin{aligned} M_{0x} &= M_0 \sin\theta \cos\phi, \\ M_{0y} &= M_0 \sin\theta \sin\phi, \\ M_{0z} &= M_0 \cos\theta. \end{aligned} \tag{55}$$

The dipole transition matrix elements are

$$\begin{aligned} R_x^{J'M'J''M''} &= M_0 \int \Psi^*_{J'M'} \sin\theta \cos\phi \Psi_{J''M''} d\tau, \\ R_y^{J'M'J''M''} &= M_0 \int \Psi^*_{J'M'} \sin\theta \sin\phi \Psi_{J''M''} d\tau, \\ R_z^{J'M'J''M''} &= M_0 \int \Psi^*_{J'M'} \cos\theta \Psi_{J''M''} d\tau, \end{aligned} \tag{56}$$

where $d\tau = \sin\theta d\theta d\phi$. Applying the recursion relation of the spherical harmonics, we can rewrite $R_z^{J'M'J''M''}$ into the following form,

$$\begin{aligned} R_z^{J'M'J''M''} = M_0 \big(a_{J'',M''} & \int Y^*_{J'M'} Y_{J''+1,M''} \sin\theta d\theta d\phi + \\ a_{J''-1,M''} & \int Y^*_{J',M'} Y_{J''-1,M''} \sin\theta d\theta d\phi \big), \end{aligned} \tag{57}$$

where

$$a_{J,M} = \sqrt{\frac{(J+1)^2 - M^2}{(2J+1)(2J+3)}}. \tag{58}$$

From the orthogonality of the spherical harmonics, we learn that the above matrix elements vanish unless $J'' = J' \pm 1$, and this is true for $R_x^{J'M'J''M''}$ and $R_y^{J'M'J''M''}$ also. Therefore the selection rule of the emission and absorption of the q-rotator model is $\Delta J = \pm 1$. The microwave and far-infrared emission (absorption) spectrum is of the wave number

$$\begin{aligned} \nu &= \frac{E_{q-rot}(J+1) - E_{q-rot}(J)}{hc}, \\ &= B\left([J+2]_q[J+1]_q - [J+1]_q[J]_q\right), \end{aligned} \tag{59}$$

where $B = \dfrac{h^2}{8\pi^2 Ihc}$.

When there is an external electric field $\vec{F}$, an induced dipole moment is formed in the molecule. Suppose that the external field is along z-axis, the induced dipole moment along the z-axis is

$$\vec{p_z} = \alpha_{zz}\vec{F_z}, \tag{60}$$

where α_{zz} is a component of the polarizability tensor in the fixed frame. When expressed in terms of the polarizability measured in the frame rotating with the molecules,

$$\alpha_{zz} = \alpha_{x_m x_m} + (\alpha_{z_m z_m} - \alpha_{x_m x_m})\cos^2\theta. \tag{61}$$

Therefore the corresponding matrix elements are

$$\begin{aligned} \int \alpha_{zz}\Psi^*_{J'M'}\Psi_{J''M''}d\tau = \quad & \alpha_{x_m x_m}\int Y^*_{J'M'}Y_{J''M''}d\tau, \\ & +(\,\alpha_{z_m z_m} - \alpha_{x_m x_m}\,)\int \cos^2\theta Y^*_{J'M'}Y_{J''M''}d\tau. \end{aligned} \tag{62}$$

According to the recursion relations of the spherical harmonics, the above equation can be written as

$$\begin{aligned} & \int \alpha_{zz}\Psi^*_{J'M'}\Psi_{J''M''}d\tau \\ & = \left\{\alpha_{x_m x_m} + (\alpha_{z_m z_m} - \alpha_{x_m x_m})\left[(a_{J'',M''})^2 + (a_{J''-1,M''})^2\right]\right\}\int Y^*_{J'M'}Y_{J''M''}d\tau \\ & +(\alpha_{z_m z_m} - \alpha_{x_m x_m})\,a_{J'',M''}a_{J''+1,M''}\int Y^*_{J'M'}Y_{J''+2,M''}d\tau \\ & +(\alpha_{z_m z_m} - \alpha_{x_m x_m})\,a_{J''-1,M''}a_{J''-2,M''}\int Y^*_{J'M'}Y_{J''-2,M''}d\tau. \end{aligned} \tag{63}$$

The first term in the above equation vanishes unless $J' = J''$, *i.e.*, it gives the lines without shift; the second and third terms vanish unless $J' = J'' \pm 2$, *i.e.*, it gives the shifted lines. The same result can be obtained for the other two components. Therefore the selection rule for the rotational Raman spectra is $\Delta J = \pm 2$. The rotational Raman spectrum of the molecules can be expressed as

$$\begin{aligned} \nu &= \nu_0 + \frac{(E_{q-\mathrm{rot}}(J+2) - E_{q-\mathrm{rot}}(J))}{hc}, \\ &= \nu_0 + B([J+3]_q[J+2]_q - [J+1]_q[J]_q), \end{aligned} \tag{64}$$

where ν_0 is the wave number of the incident photon.

The rotational spectra of diatomic molecules involve the electronic transitions and vibrational transitions with the selection rule of that of rigid rotator, *i.e.*, $\Delta J = 0, \pm 1$.

The rotational structures are

$$\begin{aligned}
R \quad \text{branch}: \quad \nu &= \nu_0 + \frac{E'_{q-\mathrm{rot}}(J+1) - E''_{q-\mathrm{rot}}(J)}{hc}, \\
&= \nu_0 + B'[J+1]_{q'}[J+2]_{q'} - B''[J]_{q''}[J+1]_{q''}; \\
Q \quad \text{branch}: \quad \nu &= \nu_0 + \frac{E'_{q-\mathrm{rot}}(J) - E''_{q-\mathrm{rot}}(J)}{hc}, \\
&= \nu_0 + B'[J+1]_{q'}[J]_{q'} - B''[J]_{q''}[J+1]_{q''}; \\
P \quad \text{branch}: \quad \nu &= \nu_0 + \frac{E'_{q-\mathrm{rot}}(J-1) - E''_{q-\mathrm{rot}}(J)}{hc}, \\
&= \nu_0 + B'[J]_{q'}[J-1]_{q'} - B''[J]_{q''}[J+1]_{q''},
\end{aligned} \tag{65}$$

where ν_0 is a quantity depending on the electronic transitions and vibrational structure of the diatomic molecules. Since internuclear distances are different for different electronic states, the I's are different. Therefore B' and B'' are different.It should be noticed that for different electronic states, we have chosen different deformation parameters in the above equation.

The infrared emission (absorption) spectrum of the q-rotator model, see (63), can be rewritten as

$$\nu = H \sinh 2\gamma(J+1) = \overline{H} \sin 2\overline{\gamma}(J+1), \tag{66}$$

where $H = \frac{B}{\sinh\gamma}$, $\overline{H} = iH$ and $\overline{\gamma} = -i\gamma$.

The rotational Raman spectrum of this model (60) can be rewritten as

$$\nu = \nu_0 + B\frac{\sinh 2\gamma(J+\frac{3}{2})}{\sinh\gamma} = \nu_0 + 2H\cosh\gamma \cdot \sinh 2\gamma\left(J + \frac{3}{2}\right). \tag{67}$$

In table 3, we give the infrared rotational absorption spectrum of the q-rotator model for the HCl molecule. The corresponding parameters of the q-rotator model in (70) are $\overline{\gamma} = 0.010744$ and $\overline{H} = 967.49(\mathrm{cm}^{-1})$. We notice that the spectrum of the q-rotator model coincides with the observed one to satisfactory accuracies.

It is noticed that the infrared emission (absorption) spectrum, rotational Raman spectrum and the rotational structures of electronic transitions and vibrations of the molecule given by the q-rotator model in (69), (70) and (71) respectively revert to the ones given by rigid rotator model when the deformation parameter q equals 1.

IV. $H_{q(J)}(4) \otimes SU(2)$ Symmetry and the Interactions

of Vibrations and Rotations

In the above sections, we suggested the models possessing $H_q(4)$ and $SU_q(2)$ quantum group symmetries to describe the vibrational and rotational structures of diatomic molecules separately, with the interaction between the two motions neglected.

However, a thorough treatment of vibrating and rotating diatomic molecules should not avoid the interactions between vibrations and rotations, with the quantum group symmetry $H_q(4) \otimes SU_{q'}(2)$, and the deformation parameters may be formal functions of the elements of the other component in the tensor product. But the nontriviality of the both components brings more ambiguities, since the simultaneous existences of q and q' introduce more parameters to the workers. Therefore from a practical point of view, we proposed the hybrid symmetry of $H_q(4) \otimes SU(2)$ with q a formal function of the Casimir operator of $SU(2)$ [27].

By assuming the deformation parameter q of $H_q(4)$ dependent on $J(J+1)$, the eigenvalues of the Casimir operator of the rotational symmetry group $SU(2)$, we supply a thorough quantum group theoretic treatment of vibrating and rotating diatomic molecules. The coincidences between the predictions of the new model and the phenomenological formulae are remarkable. It should be stressed that the dependence of deformation parameter q on the quantum number of rotation, *i.e.*, $q = q(J)$, characterizes the interaction between vibration and rotation. When $J = 0$, there is no rotational excitation and so the results of anharmonic oscillator model [24],[26] are recovered. On the other hand, when $v = 0$, there is no vibrational excitations and so the results of non-rigid rotator model [25][26] can be obtained. The results of the conventional treatments in view of rotating vibrator are reproduced by the quantum group theoretic approach, when the analytic formulae of the latter are Taylor-expanded.

We start from introduce the following kind of Hamiltonian describing the vibration in the molecule

$$H_{q(J)-\mathrm{vib}} = \frac{1}{2}\left(a^{\dagger}_{q(J)}a_{q(J)} + a_{q(J)}a^{\dagger}_{q(J)}\right) hc\nu_{vib}, \tag{68}$$

where q is a function of the eigenvalues of Casimir operator of the rotational symmetry group $SU(2)$. The deformation parameter q is no longer a constant, but rather a variable depending on the spin of the representation of the rotational symmetry group $SU(2)$ *i.e.*, $q = q(J)$. As can be seen in the following, the influence of q on rotational quantum number J is not trivial.

It is obvious that this Hamiltonian commutes with H_{rot}, the rotational Hamiltonian, *i.e.*, $H_{q(J)-vib}$ and H_{rot} have simultaneous eigenvalues. Hence the Hamiltonian that describes the vibrational and rotational spectral structures of diatomic molecules with the interaction of vibration and rotation is as follows

$$\begin{aligned} H_{vr} &= H_{q(J)-vib} + H_{rot} \\ &= \frac{1}{2}\left(a^{\dagger}_{q(J)}a_{q(J)} + a_{q(J)}a^{\dagger}_{q(J)}\right) hc\nu_{vib} + \frac{\hbar^2}{2I}C \end{aligned} \tag{69}$$

where I is the moment of inertia, and C is the Casimir operator of the $SU(2)$ algebra. The commutation relations for the new kind of q-oscillator are [28][27]

$$\begin{aligned} \left[a_{q(J)}, a^{\dagger}_{q(J)}\right] &= [N + 1 + b\gamma(J)]_{q(J)} - [N + b\gamma(J)]_{q(J)}, \\ \left[N, a_{q(J)}\right] &= -a_{q(J)}, \quad \left[N, a^{\dagger}_{q(J)}\right] = a^{\dagger}_{q(J)}. \end{aligned} \tag{70}$$

where $N = a^{\dagger}a$, and $[m]_q = \dfrac{q^m - q^{-m}}{q - q^{-1}}$. The Hopf operations: coproduct, antipode and counit can be constructed explicitly [28].

The energy levels for this system are

$$E_{q(J)-\text{vib}}(v) = \frac{1}{2}\left([v + 1 + b\gamma(J)]_{q(J)} + [v + b\gamma(J)]_{q(J)}\right) hc\nu_{\text{vib}}. \tag{71}$$

So the vibrational and rotational structure of diatomic molecules have the following form

$$E_{vr}(v, J) = \frac{1}{2}\left([v + 1 + b\gamma(J)]_{q(J)} + [v + b\gamma(J)]_{q(J)}\right) hc\nu_{\text{vib}} + \frac{\hbar^2}{2I}J(J+1). \tag{72}$$

The vibrational and rotational levels of the electronic state of diatomic molecules can be written as

$$\begin{aligned} E &= E_0 + E_{vr} \\ &= E_0 + \tfrac{\nu_{\text{vib}}}{2}\left\{[v + b(J)\gamma(J)]_{q(J)} + [v + b(J)\gamma(J) + 1]_{q(J)}\right\} hc + \frac{\hbar^2}{2I}J(J+1) \\ &= E_0 + \frac{hc\nu_{\text{vib}}}{2\sinh(\gamma(J)/2)} \sinh\left\{\gamma(J)\left(v + \tfrac{1}{2} + c(J)\right)\right\} + \frac{\hbar^2}{2I}J(J+1), \end{aligned} \tag{73}$$

where $c(J) = b(J)\gamma(J) \to 0$ if $\gamma \to 0$. When $J = 0$, there is no rotational excitation, and therefore

$$\begin{aligned} E &= E_0 + E_{q(J)-vib}(v) \\ &= E_0 + \frac{1}{2\sinh(\gamma_0/2)} \sinh\left\{\gamma_0\left(v + \frac{1}{2} + c_0\right)\right\} hc\nu_{vib}, \end{aligned} \tag{74}$$

which is just the vibrational spectrum [24][26] When $v = 0$, there is no vibrational excitation, and so

$$\begin{aligned} E &= E_0 + E_{q(J)-vib}(0) \\ &= E_0 + \frac{hc\nu_{vib}}{2\sinh(\gamma(J)/2)}\sinh\left\{\gamma(J)\left(\tfrac{1}{2} + c(J)\right)\right\} \\ &\quad + \frac{\hbar^2}{2I}J(J+1), \end{aligned} \tag{75}$$

which coincides with the leading terms in the formula of the q-rotator model possessing $SU_q(2)$ symmetry. It should be noticed that when $v = J = 0$, we have

$$E = E_0 + \frac{1}{2\sinh(\gamma(0)/2)}\sinh\left\{\gamma(0)\left(\frac{1}{2} + c(0)\right)\right\} hc\nu_{vib} \tag{76}$$

which is T_e, the electronic term.

Although γ and c are undetermined functions of J, we suppose they are in the following forms for simplicity

$$\begin{aligned} \gamma(J) &= \gamma_0 + \gamma_1 J(J+1), \\ c(J) &= c_0 + c_1 J(J+1), \end{aligned} \tag{77}$$

then we have

$$\begin{aligned} E &= E_0 + \frac{1}{2\sinh\left(\frac{1}{2}\gamma_0 + \frac{1}{2}\gamma_1 J(J+1)\right)} \\ &\quad \cdot \sinh\left\{(\gamma_0 + \gamma_1 J(J+1))\left(v + \tfrac{1}{2} + c_0 + c_1 J(J+1)\right)\right\} hc\nu_{vib} \\ &\quad + \frac{\hbar^2}{2I}J(J+1). \end{aligned} \tag{78}$$

The above equation is the general form of the vibrational rotational energy levels of the diatomic molecule. The second term indicates the vibrational spectra with the interaction of the rotational and vibrational motions, while the third describes the rigid rotation. The total Hamiltonian for this system is

$$H = H_e + H_{q(J)-vib} + H_{\mathrm{rot}}, \tag{79}$$

which bears the symmetry of $H_q(4) \otimes SU(2)$, therefore the Hilbert space should be constructed from the representations of the algebra $H_q(4) \otimes SU(2)$, *i.e.*,

$$\Psi_{vr} = N_v H_v(X) e^{-X^2/2} Y_{JM}(\theta, \phi), \tag{80}$$

As given in [24][25][26][27], the selection rule for infrared spectrum of the model with $H_q(4) \otimes SU(2)$ symmetry is identical to the model with $H(4) \otimes SU(2)$ symmetry, *i.e.*, v can change by any integral amount although $\Delta v = \pm 1$ gives the most intense transitions, and J can change only by unity. Of course $\Delta v = 0$ is also allowed, but this does not give rise to any rotational and vibrational spectrum but rather the pure rotational one. If we now consider a particular transition from v' to v'', the spectrum (in wavenumber) should be

$$\begin{aligned} \nu &= \frac{\nu_{\text{vib}}}{2}\left[2\left(v' + \frac{1}{2} + c_0 + c_1 J'(J'+1)\right)\right]_{\langle(\gamma_0+\gamma_1 J'(J'+1))/2\rangle} \\ &\quad -\frac{\nu_{\text{vib}}}{2}\left[2\left(v'' + \frac{1}{2} + c_0 + c_1 J''(J''+1)\right)\right]_{\langle\gamma_0+\gamma_1 J''(J''+1))/2} \\ &\quad +B_e\left\{J'(J'+1) - J''(J''+1)\right\}, \end{aligned} \tag{81}$$

where $B_e = \frac{\hbar}{4\pi I c}$ and the notation $[x]_{\langle\gamma\rangle} = [x]_q$ is applied for brevity.

From the selection rule $\Delta J = 1$ or -1, we have

$$\begin{aligned} \nu_R &= \frac{\nu_{\text{vib}}}{2}\left[2\left(v' + \tfrac{1}{2} + c_0 + c_1 (J+1)(J+2)\right)\right]_{\langle(\gamma_0+\gamma_1 (J+1)(J+2))/2\rangle} \\ &\quad -\frac{\nu_{\text{vib}}}{2}\left[2\left(v'' + \tfrac{1}{2} + c_0 + c_1 J(J+1)\right)\right]_{\langle(\gamma_0+\gamma_1 J(J+1))/2\rangle} \\ &\quad +B_e\left\{(J+1)(J+2) - J(J+1)\right\}; \end{aligned} \tag{82}$$

and

$$\begin{aligned} \nu_P &= \frac{\nu_{\text{vib}}}{2}\left[2\left(v' + \tfrac{1}{2} + c_0 + c_1 J(J-1)\right)\right]_{\langle(\gamma_0+\gamma_1 J(J-1))/2\rangle} \\ &\quad -\frac{\nu_{\text{vib}}}{2}\left[2\left(v'' + \tfrac{1}{2} + c_0 + c_1 J(J+1)\right)\right]_{\langle(\gamma_0+\gamma_1 J(J+1))/2\rangle} \\ &\quad +B_e\left\{J(J-1) - J(J+1)\right\}, \end{aligned} \tag{83}$$

where J'' is replaced by J. Since J can take a whole series of values, these two formulae represent two series of lines, which are called the R and P branches respectively.

The selection rules for the Raman spectrum are just those obtained in the model of linear oscillator and rigid rotator. The selection rule for the former is the same as for the infrared spectrum, while for the latter is $\Delta J = 0, \pm 1$. Accordingly for a given vibrational transition, *i.e.*, a given Raman vibrational band, there are three branches. Their formulae are readily obtained from

$$\begin{aligned} \Delta\nu &= \frac{\nu_{\text{vib}}}{2}\left[2\left(v' + \frac{1}{2} + c_0 + c_1 J'(J'+1)\right)\right]_{\langle(\gamma_0+\gamma_1 J'(J'+1))\rangle} \\ &\quad -\frac{\nu_{\text{vib}}}{2}\left[2\left(v'' + \frac{1}{2} + c_0 + c_1 J''(J''+1)\right)\right]_{\langle(\gamma_0+\gamma_1 J''(J''+1))/2\rangle} \\ &\quad +B_e\left\{J'(J'+1) - J''(J''+1)\right\}, \end{aligned} \tag{84}$$

by substituting $J' = J'' + 2$ (S branch), $J' = J'' - 2$ (O branch) and $J' = J''$ (Q branch) and redenoting $J'' = J$:

$$\begin{aligned}(\Delta\nu)_S &= \frac{\nu_{\text{vib}}}{2}\left[2\left(v' + \frac{1}{2} + c_0 + c_1(J+2)(J+3)\right)\right]_{\langle(\gamma_0+\gamma_1(J+2)(J+3))/2\rangle} \\ &\quad -\frac{\nu_{\text{vib}}}{2}\left[2\left(v'' + \frac{1}{2} + c_0 + c_1 J(J+1)\right)\right]_{\langle(\gamma_0+\gamma_1 J(J+1))/2\rangle} \\ &\quad +B_e(4J+6), \qquad J = 0, 1, \cdots;\end{aligned} \tag{85}$$

$$\begin{aligned}(\Delta\nu)_O &= \frac{\nu_{\text{vib}}}{2}\left[2\left(v' + \frac{1}{2} + c_0 + c_1(J-2)(J-1)\right)\right]_{\langle(\gamma_0+\gamma_1(J-2)(J-1))/2\rangle} \\ &\quad -\frac{\nu_{\text{vib}}}{2}\left[2\left(v'' + \frac{1}{2} + c_0 + c_1 J(J+1)\right)\right]_{\langle(\gamma_0+\gamma_1 J(J+1))/2\rangle} \\ &\quad +B_e(-4J+2), \qquad J = 2, 3, \cdots;\end{aligned} \tag{86}$$

and

$$\begin{aligned}(\Delta\nu)_Q &= \frac{\nu_{\text{vib}}}{2}\left[2\left(v' + \frac{1}{2} + c_0 + c_1 J(J+1)\right)\right]_{\langle(\gamma_0+\gamma_1 J(J+1))/2\rangle} \\ &\quad -\frac{\nu_{\text{vib}}}{2}\left[2\left(v'' + \frac{1}{2} + c_0 + c_1 J(J+1)\right)\right]_{\langle(\gamma_0+\gamma_1 J(J+1))/2\rangle}, \qquad J = 0, 1, \cdots.\end{aligned} \tag{87}$$

Now we observe the vibrational and rotational structure involving electronic transitions, for which the spectrum is

$$\nu = \left(E_0' - E_0'' + E_{q(J)-vib}' - E_{q(J)-vib}'' + E_{rot}' - E_{rot}''\right)/hc, \tag{88}$$

where E_0', $E_{q(J)-vib}'$, E_{rot}' and E_0'', $E_{q(J)-vib}''$, E_{rot}'' are the electronic energy and the vibrational rotational terms of the upper and lower electronic states respectively. $E_{q(J)-vib}'$, E_{rot}' and $E_{q(J)-vib}''$, E_{rot}'' belong to different electronic states. The selection rules to be applied in the present case are those of the symmetric top. Unlike the case of infrared spectra, the present upper and lower states may have different electronic angular momenta Λ. If at least one of the two states has nonzero Λ, then the selection rule for J is $\Delta J = J' - J'' = 0, \pm 1$. However, if $\Lambda = 0$ in both electronic states, (*i.e.*, the transition is $^1\Sigma \rightarrow {}^1\Sigma$), the transition with $\Delta J = 0$ is forbidden and only the transitions with $\Delta J = \pm 1$ appear, as for most infrared bands. Thus we expect to have three or two series of lines (branches), whose wavenumbers are given by the following formulae respectively

R branch :

$$\begin{aligned}\nu &= \frac{E_0' - E_0''}{hc} \\ &+ \frac{\nu_{\text{vib}}'}{2}\left[2\left(v' + \frac{1}{2} + c_0' + c_1'(J+1)(J+2)\right)\right]_{\langle(\gamma_0'+\gamma_1'(J+1)(J+2))/2\rangle} \\ &- \frac{\nu_{\text{vib}}''}{2}\left[2\left(v'' + \frac{1}{2} + c_0'' + c_1''J(J+1)\right)\right]_{\langle(\gamma_0''+\gamma_1''J(J+1))/2\rangle} \\ &+ \left\{B_e'(J+2)(J+1) - B_e''J(J+1)\right\}; \end{aligned} \tag{89}$$

and

Q branch :

$$\begin{aligned}\nu &= \frac{E_0' - E_0''}{hc} \\ &+ \frac{\nu_{\text{vib}}'}{2}\left[2\left(v' + \frac{1}{2} + c_0' + c_1'J(J+1)\right)\right]_{\langle(\gamma_0'+\gamma_1'J(J+1))/2\rangle} \\ &- \frac{\nu_{\text{vib}}''}{2}\left[2\left(v'' + \frac{1}{2} + c_0'' + c_1''J(J+1)\right)\right]_{\langle(\gamma_0''+\gamma_1''J(J+1))/2\rangle} \\ &+ \left(B_e' - B_e''\right)J(J+1); \end{aligned} \tag{90}$$

and

P branch :

$$\begin{aligned}\nu &= \frac{E_0' - E_0''}{hc} \\ &+ \frac{\nu_{\text{vib}}'}{2}\left[2\left(v' + \frac{1}{2} + c_0' + c_1'(J-1)J\right)\right]_{\langle(\gamma_0'+\gamma_1'(J-1)J)/2\rangle} \\ &- \frac{\nu_{\text{vib}}''}{2}\left[2\left(v'' + \frac{1}{2} + c_0'' + c_1''J(J+1)\right)\right]_{\langle(\gamma_0''+\gamma_1''J(J+1))/2\rangle} \\ &+ \left\{B_e'(J-1)J - B_e''J(J+1)\right\}. \end{aligned} \tag{91}$$

Now, we have a complete description of vibrating and rotating diatomic molecules by the model suggested. Rewrite energy spectrum in (78) into the following

$$\begin{aligned}\nu &= A + B\sinh\left\{(\gamma_0 + \gamma_1 J(J+1))\left(v + \tfrac{1}{2} + c_0 + c_1 J(J+1)\right)\right\} \\ &+ B_e J(J+1) \end{aligned} \tag{92}$$

where we denote $A = \frac{E_0}{hc}$, $B = \frac{\nu_{\mathrm{vib}}}{2\sinh\left(\frac{1}{2}\gamma_0 + \frac{1}{2}\gamma_1 J(J+1)\right)}$.

In table 4, we give parameters A, B, c_0, c_1 and γ_0, γ_1 in the model for some randomly selected molecules and states. If one Taylor expands (92), the parameters in the usual rotating oscillator model, T_e, ω_e, $\omega_e x_e$, $\omega_e y_e$ and α_e are reproduced. In table 5, we show these parameters computed for the molecules and states listed in table 4. It should be noticed that the data in table 3 coincide with the empirical ones accurately [21].

In (77), we only demonstrated the linear term of $J(J+1)$, but ignored the higher order terms of $J(J+1)$. If we consider the contributions of terms of higher orders are taken into account, more accurate results will be obtained to describe the vibration-rotational structures,

$$\begin{aligned} \gamma(J) &= \gamma_0 + \gamma_1 J(J+1) + \gamma_2 \left(J(J+1)\right)^2, \\ c(J) &= c_0 + c_1 J(J+1) + c_2 \left(J(J+1)\right)^2, \end{aligned} \tag{93}$$

The Taylor expansion of the energy level formula reproduces T_e, ω_e, $\omega_e x_e$, $\omega_e y_e$ and α_e, β_e and D_e accurately. In table 6, we give parameters A, B, γ_0, γ_1, γ_2 and c_0, c_1, c_2 for some randomly selected molecules and states. Table 7 lists the leading terms of the Taylor expansions, computed for the indicated states of particular molecules. All the data coincide with experimental ones very satisfactorily [21][22].

V. Discussions and Remarks

Quantum group as a beautiful mathematical structure has been applied in some quantum systems, such as the exactly solved statistical models, integrable quantum systems and conformal field theories in recent years. More and more physicists pay attentions to possible applications of quantum groups in other fields, for they are potential dynamical symmetries in the extensions of the above theories. In this paper, we stressed the possibility that the vibrational and rotational structures in diatomic molecules can be described phenomenologically by quantum groups. The vibrating and rotating diatomic molecule can be described by quantum group theoretic approach compactly. All the results of anharmonic oscillator plus rigid rotator model and vibrating rotator model can be reproduced from the Taylor expansions of the analytic formulae of the quantum group theoretic approach. The fitting of the approach with experimental data is satisfactory.

The Dunham phenomenological formula for vibrational excitations stimulates one to propose the following Hamiltonian for the molecule in obviously the most direct way,

$$h_{vib} = hc\omega_e\left(N+\frac{1}{2}\right) - hc\omega_e x_e\left(N+\frac{1}{2}\right)^2 + hc\omega_e y_e\left(N+\frac{1}{2}\right)^3 + \cdots. \tag{94}$$

This Hamiltonian describes a system with nonlinear potential depending on the energy level. If one rewrites h_{vib} into coordinates, one obtains

$$h_{vib} = -\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + \hat{V}, \tag{95}$$

and

$$\hat{V} = \frac{1}{2}(2\pi\omega_e c)mx^2 - hc\omega_e x_e\left(N+\frac{1}{2}\right)^2 + hc\omega_e y_e\left(N+\frac{1}{2}\right)^3 + \cdots. \tag{96}$$

It is obvious that $\hat{V}$ is the pseudo-potential that depends on the energy eigenvalues. This point is clear if we rewrites the Schrödinger equation into

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi(x)}{\partial x^2} + V_{eff}(x)\psi(x) = E\psi(x), \tag{97}$$

where $V_{eff}(x) = \left(\hat{V}\psi\right)\psi^{-1}$ is the effective potential. The pseudo-potential is currently a common concept frequently applied in theories of nuclear physics, and its dependence on the states reveals a general feature of the dynamical nonlinearities in the realistic systems.

The conventional model of nonlinear oscillator applied to explain the Dunham formula (9) (without rotational excitation) introduces local potential of the following type

$$U = \frac{1}{2}m\left(2\pi\omega_e c\right)^2 x^2 + ax^3 + bx^4 + \cdots, \tag{98}$$

where

$$a = \frac{1}{6}\left(\frac{d^3U}{dx^3}\right)_{r=r_e}, \quad b = \frac{1}{24}\left(\frac{d^4U}{dx^4}\right)_{r=r_e}. \tag{99}$$

The energy eigenvalues are obtained by 2-nd order perturbation (to reproduce x_e) and 3-rd order perturbation (to reproduce y_e), while the wavefunctions of the linear oscillator are modified by 1-st and 2-nd order perturbations. As we require that the energy spectra and the selection rules of the pseudo-potential model and the local potential model coincide, these two models are essentially identically effective, if one ignores the differences between the the wavefunctions of the pseudo-potential model (which are just those of the linear oscillator) and those of the local potential model (which are the wavefunctions of the linear oscillator modified by 1-st and/or 2-nd order perturbations). Because the small differences between the wavefunctions yielded from the two models are difficult to detect experimentally (if not in principle), one has the freedom to favour either of the models. After all, we stress that the new Hamiltonian in (94) is the most direct conjecture from the Dunham formula (9), and is therefore meaningfull to be inverstigated, if one is not prejudiced against models involving pseudo-potentials. The Hamiltonian (94) is invariant under transformations of quantum symmetries[6].

It should be emphasized that the Yang-Baxter equations associate to the quantum groups are certainly (rather hidden) symmetries of the diatomic system, this is an interesting topic without explicit formulation. The quantum groups' induced currents should also be found and explored in the newly set-up model, which may reveal some hidden nature of the molecule. We hope the forth coming works along these lines will support or finally verify definitely our idea that the quantum group symmetries are dynamical symmetries in the system of the diatomic molecule, in other words, the treatments presented in this paper are not merely phenomenological ones.

It is also worth noting that the nuclear shell model can also be extended by replacing some or all of the three components by the q-deformed harmonic oscillator(s), and the extended model will certainly give exact descriptions to the violations of the spherical symmetry of the spherically symmetric system and the equidistancy of the energy levels, and therefore may be an *exactly solvable* model suitable in dealing with the structures of some deformed nuclei.

We end this paper by remarking that this quantum group theoretic approach can be possibly applied in other fields of physics, such as the quasi-molecular structures in heavy-ion resonances [29][30], which will be dealt with in our forth coming publication; and the non-linear vibrations in the hydrogen bonds which are conventionally approximated by the effective potentials of forms of Toda lattice potential, Lennard-Jones potential and $2-3$ potential [31]. This new approach will bring exact solutions of wavefunctions and energy levels to the considered systems, provided that the quantum group symmetries are shown qualified as dynamical symmetries of these systems where the $SU(2)$ symmetry is apparently broken.

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[6] There may be such opinion that (94) is also invariant under the transformations of universal enveloping Lie algebras, but actually the latter would introduce infinite free parameters, and therefor useless if not meaningless.

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Table captions

Table 1. The parameters are determined phenomenologically for the spectra of the q-oscillator model to meet the vibrational spectra of some diatomic molecules randomly selected.

Table 2. The parameters T_e, ω_e, $\omega_e x_e$ and $\omega_e y_e$ reproduced. They meet the observed values [21][22][23] very accurately.

Table 3. The comparison of the observed and calculated values for HCl absorption spectrum in the far infrared. The parameter $\overline{\gamma}$ is 0.010744 and $\overline{H} = 967.49(\mathrm{cm}^{-1})$.

Table 4. The parameters are computed for the energy spectra of the q-oscillator model to meet the vibrational energy spectra of some diatomic molecules and their particular states randomly selected.

Table 5. The parameters T_e, ω_e, $\omega_e x_e$, $\omega_e y_e$ and α_e reproduced. They meet the observed values [21][22][23] very accurately.

Table 6. When the dependences of γ and c on the rotational quantum number J is modified by $(J(J+1))^2$ terms, the parameters are computed for the energy spectra of the q-oscillator model.

Table 7. The parameters T_e, ω_e, $\omega_e x_e$, $\omega_e y_e$, α_e, β_e and D_c reproduced. They can be seen to meet the observed values [22] very accurately.

Table 1.

Molecule	State	E_0/hc	H/hc	γ	c
$Ag^{107}Cl^{35}$	B $^3\Pi_{0+}$	25691.13	$8597.85i$	$-0.0450385i$	16.8479
$Al^{27}Br^{79}$	A $^1\Pi$	34676.41	$3122.41i$	$-0.103147i$	3.83473
$Al^{27}Cl^{35}$	A $^1\Pi$	35219.55	$8916.37i$	$-0.0536680i$	6.47054
$Al^{27}F^{19}$	A $^1\Pi$	31466.82	$25536.31i$	$-0.0369252i$	13.8141
$B^{11}Br^{79}$	A $^1\Pi$	37332.13	5266.95	0.101739	−5.96596
$(Be^9H^2)^+$	A $^1\Sigma^+$	20023.45	$41821.13i$	$-0.0295903i$	16.2950
Bi_2^{209}	B	−10233.77	$39940.40i$	$-0.00463802i$	167.317
$Bi^{209}Br^{79}$	A	20297.13	$2029.14i$	$-0.0674324i$	1.72040
$Bi^{209}Cl^{35}$	B	26769.70	8812.56	0.0396838	−10.5809
C_2^{12}	c $^1\Pi_g$	31890.27	$15846.18i$	$-0.115467i$	1.30107
C_2^{12}	B $^3\Pi_g$	−33.48	$-47485.83i$	$-0.041233i$	10.1732
$Ca^{40}F^{19}$	A $^2\Pi$	27407.16	20958.81	0.0250473	−19.9682
$(Cl_2^{35})^+$	A $^2\Pi$	135.29	$34769.24i$	$-0.0200919i$	31.3161
$Cl^{35}F^{19}$	A $^3\Pi_{0+}$	18376.85	$3629.20i$	$-0.0874985i$	1.83165
$C^{12}O^{16}$	c $^3\Pi_i$	36597.15	$53317.40i$	$-0.0243568i$	20.6515
Cs_2^{133}	B $(^1\Pi_u)$	8313.06	$7610.36i$	$-0.00574204i$	116.826
Cs_2^{133}	X $^1\Sigma_g$	−6819.43	$11027.52i$	$-0.00485309i$	137.598
$Cs^{133}H^1$	A $^1\Sigma^+$	19512.63	$2295.45i$	$-0.101460i$	−4.96200

Table 2.

Molecule	State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$
$Ag^{107}Cl^{35}$	B $^3\Pi_{0+}$	31606.92	281.0	6.00	−0.095
$Al^{27}Br^{79}$	A $^1\Pi$	35879.5	297.2	6.40	−0.527
$Al^{27}Cl^{35}$	A $^1\Pi$	38254.0	449.96	4.37	−0.216
$Al^{27}F^{19}$	A $^1\Pi$	43935	822.9	8.5	−0.187
$B^{11}Br^{79}$	A $^1\Pi$	33935.3	637.63	17.58	1.1
$(Be^9H^2)^+$	A $^1\Sigma^+$	39416.2	1096.41	8.49	−0.16
Bi_2^{209}	B	17742.3	132.21	0.3009	−0.000474
$Bi^{209}Br^{79}$	A	20532.0	135.91	0.534	−0.1030
$Bi^{209}Cl^{35}$	B	22959.7	381.0	3.00	0.10
C_2^{12}	c $^1\Pi_g$	34261.9	1809.1	15.81	−4.02
C_2^{12}	B $^3\Pi_g$	19306.26	1788.22	16.44	−0.5067
$Ca^{40}F^{19}$	A $^2\Pi$	16482.1	592.0	3.427	0.0619
$(Cl_2^{35})^+$	A $^2\Pi$	20596.9	564.8	4.13	−0.038
$Cl^{35}F^{19}$	A $^3\Pi_{0+}$	18956	313.48	2.217	−0.400
$C^{12}O^{16}$	c $^3\Pi_i$	62299.4	1137.79	7.624	−0.1125
Cs_2^{133}	B $(^1\Pi_u)$	13043.87	34.230	0.07799	−0.0001881
Cs_2^{133}	X $^1\Sigma_g$	0.	41.990	0.08005	−0.0001643
$Cs^{133}H^1$	A $^1\Sigma^+$	18405.2	204.0	−5.70	−0.350

Table 3.

J	ν^{exp} (cm^{-1})	ν^{the}	$\nu^{exp} - \nu^{the}$
0	$\cdots$	20.79	$\cdots$
1	$\cdots$	41.57	$\cdots$
2	$\cdots$	62.33	$\cdots$
3	83.03	83.06	−0.03
4	(104.1)	103.75	0.35
5	124.3	124.39	−0.1
6	145.03	144.98	0.05
7	165.51	165.50	0.01
8	185.86	185.95	−0.09
9	206.38	206.30	0.08
10	226.50	226.57	−0.07

Table 4.

Molecule	State	A	B	γ_0
$Au^{197}H^1$	$A\ ^1\Sigma+$	19868.80	16067.03	0.1188428
$Au^{197}H^1$	$X\ ^1\Sigma+$	−752970.26	783168.35	1.0702055^{-2}
$Au^{197}H^2$	$X\ ^1\Sigma+$	−409785.87	439564.55	1.0280537^{-2}
$(Be^9H^1)^+$	$A\ ^1\Sigma^+$	−152217.04	225454.84	1.2428298^{-2}
$(Be^9H^1)^+$	$X\ ^1\Sigma^+$	−1403198.58	1433874.68	7.5308293^{-3}
$(Cl_2^{35})^+$	$A\ ^2\Pi$	−57270.29	92182.84	1.1674449^{-2}
$(Cl_2^{35})^+$	$A\ ^2\Pi$	134.68596	34769.237	2.0091848^{-2}
$(C^{12}O^{16})^+$	$B\ ^2\Sigma^+$	95049.22	15154.84	3.370260^{-2}
$(C^{12}O^{16})^+$	$X\ ^2\Sigma^+$	−88949.22	169548.88	1.3772479^{-3}
$(Mg^{24}H^2)^+$	$A\ ^1\Sigma^+$	27825.20	29018.47	2.931283^{-2}
$(Mg^{24}H^2)^+$	$X\ ^1\Sigma^+$	−39907.35	58603.67	2.858133^{-2}

Table 4. (continued)

Molecule	State	γ_1	c_0	c_1
$Au^{197}H^1$	$A\ ^1\Sigma+$	-3.43^{-6}	4.263415	-1.15^{-5}
$Au^{197}H^1$	$X\ ^1\Sigma+$	-4.34^{-10}	120.74304	-8.35^{-6}
$Au^{197}H^2$	$X\ ^1\Sigma+$	-3.71^{-10}	116.78317	-4.83^{-6}
$(Be^9H^1)^+$	$A\ ^1\Sigma^+$	-2.51^{-9}	81.746397	-9.71^{-6}
$(Be^9H^1)^+$	$X\ ^1\Sigma^+$	-1.66^{-10}	181.06518	-9.91^{-6}
$(Cl_2^{35})^+$	$A\ ^2\Pi$	-1.31^{-10}	86.521301	-5.62^{-7}
$(Cl_2^{35})^+$	$A\ ^2\Pi$	-1.14^{-9}	31.316138	-2.80^{-7}
$(C^{12}O^{16})^+$	$B\ ^2\Sigma^+$	-1.18^{-8}	−56.17106	-5.10^{-5}
$(C^{12}O^{16})^+$	$X\ ^2\Sigma^+$	0.00^{-10}	1067.7671	-3.67^{-7}
$(Mg^{24}H^2)^+$	$A\ ^1\Sigma^+$	-1.44^{-7}	9.622465	-1.29^{-6}
$(Mg^{24}H^2)^+$	$X\ ^1\Sigma^+$	-2.46^{-8}	26.20894	-5.45^{-6}

Table 5.

Molecule	State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	α_e
$Au^{197}H^1$	$A\ ^1\Sigma^+$	27665.7	1669.55	55.06	−3.93	0.249
$Au^{197}H^1$	$X\ ^1\Sigma^+$	0.0	2305.01	43.12	−0.044	0.2136
$Au^{197}H^2$	$X\ ^1\Sigma^+$	0.0	1634.98	21.655	−0.0288	0.07614
$(Be^9H^1)^+$	$A\ ^1\Sigma^+$	39417.0	1476.1	14.8	−0.038	0.1249
$(Be^9H^1)^+$	$X\ ^1\Sigma^+$	0.0	2221.7	39.79	−0.021	0.2935
$(Cl_2^{35})^+$	$A\ ^2\Pi$	20797.3	572.3	5.32	−0.013	0.0028
$(Cl_2^{35})^+$	$A\ ^2\Pi$	20596.9	564.8	4.13	−0.038	0.0017
$(C^{12}O^{16})^+$	$B\ 2\Sigma^+$	45876.7	1734.18	27.927	0.3283	0.03025
$(C^{12}O^{16})^+$	$X\ 2\Sigma^+$	0.0	2214.24	15.164	−0.0007	0.01896
$(Mg^{24}H^2)^+$	$A\ ^1\Sigma^+$	35902.1	817.0	3.47	−0.117	0.023
$(Mg^{24}H^2)^+$	$X\ ^1\Sigma^+$	0.0	1226.6	16.3	−0.167	0.064

Table 6.

Molecule	State	A	B	γ_0	γ_1	γ_2
KD	$A\ ^1\Sigma$	16635.94	3943.851	5.17837^{-2}	-1.74^{-7}	-7.94^{-12}
$La^{139}O^{16}$	$C\ ^2\Pi_{1/2}$	63859.96	52289.1	1.18996^{-2}	-3.73^{-10}	3.8^{-15}
$La^{139}O^{16}$	$A'\ ^2\Delta_{5/2}$	71773.46	43052.08	1.00781^{-2}	-1.53^{-10}	1.20^{-15}
$La^{139}O^{16}$	$A'\ ^2\Delta_{3/2}$	28273.81	42532.06	1.72647^{-2}	-1.51^{-9}	1.17^{-14}
$La^{139}O^{16}$	$A\ ^4\Sigma^+$	20780.41	42532.06	1.72647^{-2}	-1.32^{-9}	-9.70^{-16}

Table 6.(continued)

Molecule	State	c_0	c_1	c_2
KD	$A\ ^1\Sigma$	12.78199	-7.61^{-6}	1.85^{-9}
$La^{139}O^{16}$	$C\ ^2\Pi_{1/2}$	-60.8124	-2.75^{-7}	1.70^{-12}
$La^{139}O^{16}$	$A'\ ^2\Delta_{5/2}$	-117.2722	-5.33^{-7}	3.13^{-12}
$La^{139}O^{16}$	$A'\ ^2\Delta_{3/2}$	-27.27976	-1.625^{-7}	-2.96^{-13}
$La^{139}O^{16}$	$A\ ^4\Sigma^+$	-27.27976	-1.421^{-7}	-1.47^{-12}

Table 7.

Molecule	State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	α_e	D_e	β_e
KD	$A\ ^1\Sigma$	19059.9	161.1	3.25	-0.0720	0.0127	2.7^{-5}	0.0^{-10}
$La^{139}O^{16}$	$C\ ^2\Pi_{1/2}$	22631.3	792.37	2.919	0.0187	0.0016	2.97^{-7}	-3.5^{-8}
$La^{139}O^{16}$	$A'\ ^2\Delta_{5/2}$	8190.1	773.87	3.229	0.0131	0.0016	2.94^{-7}	-2.7^{-8}
$La^{139}O^{16}$	$A'\ ^2\Delta_{3/2}$	7493.4	817.26	3.097	0.0406	0.0016	2.94^{-7}	-2.7^{-8}
$La^{139}O^{16}$	$A\ ^4\Sigma^+$	0	817.26	3.097	0.0406	0.0014	2.6^{-7}	0.0^{-10}