

q -Deformed Boson-Realization Model Applied to Vibrational Spectrum of Sulfur Dioxide

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A q -deformed boson-realization model is presented to study both stretching and bending vibrations of sulfur dioxide, where Fermi resonances are taken into account. Our results are compared with those of other models.

In recent years, quantum groups (or algebras) have been extensively used for describing the vibrational and rotational spectra of diatomic molecules. For this purpose, for example, $H_q(4)$ and $SU_q(2)$ models (Chang, 1995) as well as the q -deformed vibron model (Alvarez *et al.*, 1994) have been used. The vibrations of diatomic molecules were also analyzed in terms of $U_q(2)$, $SU_q(1, 1)$ (Bonatsos *et al.*, 1992) and $U_q(4)$ (Gupta and Cooper, 1995). The rotational spectra were successfully explained in terms of the quantum algebra $su_q(2)$ (Chang, 1995; Bonatsos *et al.*, 1990). In addition, a q -deformed formalism of the $SU(2)$ algebraic model (Bonatsos and Daskaloyannis, 1993) was proposed for the stretching vibrations of polyatomic molecules (Iachello and Oss, 1991). Recently, we studied the stretching and the bending vibrations of methane in the boson-realization model (Ma *et al.*, 1996) and in terms of q -deformed harmonic oscillators instead of Morse ones (Xie *et al.*, 1996). In the present paper we construct a q -deformed boson-realization model for the complete vibrations of bent triatomic molecules, where Fermi resonances between the stretching and the bending vibrations are considered. As an example, we apply it to the vibrations of sulfur dioxide.

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We introduce three sets of q -deformed boson operators a_i^\dagger (a_i) ($1 \leq i \leq 2$) and a_3^\dagger (a_3) to describe the stretching and the bending modes of XY_2 , respectively. Each set of operators satisfies the relations

$$\begin{aligned} [a_i, N_i] &= a_i, & [a_i^\dagger, N_i] &= -a_i^\dagger \\ a_i^\dagger a_i &= [N_i], & a_i a_i^\dagger &= [N_i + 1] \end{aligned} \quad (1)$$

where $[N_i]$ is the structure function, a positive analytic function with $[0] = 0$, and N_i is the number operator. The deformed algebra possesses a Fock space of eigenvectors $|n_i\rangle$ of the number operator N_i :

$$N_i |n_i\rangle = n_i |n_i\rangle, \quad \langle n_i | m_i \rangle = \delta_{nm} \quad (2)$$

In fact, $|n_i\rangle$ can be defined from the vacuum state $|0\rangle$:

$$|n_i\rangle = ([n_i]!)^{-1/2} (a_i^\dagger)^{n_i} |0\rangle, \quad [n_i]! = \sum_{k=1}^{n_i} [k] \quad (3)$$

The generators a_i^\dagger and a_i are the creation and annihilation operators of this q -deformed algebra, respectively:

$$a_i |n_i\rangle = [n_i]^{1/2} |n_i - 1\rangle, \quad a_i^\dagger |n_i\rangle = [n_i + 1]^{1/2} |n_i + 1\rangle \quad (4)$$

Various schemes of deformed oscillator algebras with different structure functions are equivalent to each other from the algebraic viewpoint. Denote the structure function $[n]_s$ ($= [N_1] = [N_2]$) for the stretching modes and $[n]_b$ ($= [N_3]$) for the bending modes. For convenience, we choose the first scheme (Arik and Coon, 1976), where

$$[n]_s = (q_s^n - 1)/(q_s - 1), \quad [n]_b = (q_b^n - 1)/(q_b - 1) \quad (5)$$

It is obvious that $[n]_s$ is real if q_s is real, and for a positive integer n , $[n]_s < n$ if $0 < q_s < 1$, and $[n]_s > n$ if $1 < q_s$, and similarly for $[n]_b$.

Due to Fermi resonances, the "total number" of phonons $N_1 + N_2 + N_3/2$ is a preserved quantity. Neglecting the mixture of the states with different total number of phonons, and taking interactions up to the fifth order, we can express the Hamiltonian in terms of the q -deformed boson operators as follows:

$$H = H_s + H_b + H_f + H_{sb} + H_{fsb} \quad (6)$$

where

$$\begin{aligned} H_s &= \sum_{i=1}^2 \omega_s a_i^\dagger a_i (1 + x_s a_i a_i^\dagger) + \lambda_{s1} (a_1^\dagger a_2 + a_2^\dagger a_1) + \lambda_{s2} (a_1^\dagger a_1 a_2^\dagger a_2) \\ &+ \lambda_{s3} (a_1^\dagger a_1 a_2 a_2^\dagger + \text{H.c.}) + \lambda_{s4} \{ (a_1^\dagger a_2 + a_2^\dagger a_1) (a_1^\dagger a_1 + a_2^\dagger a_2) + \text{H.c.} \} \end{aligned}$$

$$\begin{aligned}
 H_b &= \omega_b a_3^\dagger a_3 (1 + x_b a_3 a_3^\dagger) \\
 H_f &= \lambda_f \{ (a_1^\dagger + a_2^\dagger) a_3 a_3 + \text{H.c.} \} \\
 H_{sb} &= \lambda_{sb1} (a_1^\dagger a_2 + a_2^\dagger a_1) a_3^\dagger a_3 + \lambda_{sb2} (a_1^\dagger a_1 + a_2^\dagger a_2) a_3^\dagger a_3 \\
 H_{fsb} &= \lambda_{fsb1} \{ a_1^\dagger a_2^\dagger (a_1 + a_2) a_3 a_3 + \text{H.c.} \} \\
 &\quad + \lambda_{fsb2} \{ (a_1^\dagger a_1^\dagger a_1 + a_2^\dagger a_2^\dagger a_2) a_3 a_3 + \text{H.c.} \} \\
 &\quad + \lambda_{fsb3} \{ (a_1^\dagger a_1^\dagger a_2 + a_2^\dagger a_2^\dagger a_1) a_3 a_3 + \text{H.c.} \} \\
 &\quad + \lambda_{fsb4} \{ (a_1^\dagger + a_2^\dagger) a_3^\dagger a_3 a_3 + \text{H.c.} \}
 \end{aligned}$$

where H_s describes the second- and the fourth-order interactions between the stretching vibrations, and H_b describes the interactions between the bending ones. ω and x are used for comparing them with the constants in the Morse potential, and their subscripts s and b refer to the stretching and the bending modes. H_f is the Fermi resonance between the stretching and the bending vibrations, H_{sb} the fourth-order interaction between the stretch and the bend, and H_{fsb} the fifth-order interaction due to Fermi resonances. All λ 's with subscripts are the coupling constants.

Some other models can be obtained when $q_s = q_b = 1$ in Eq. (6). H_s is the $SU(2)$ model (Kellman, 1985) describing two stretching bonds. This kind of Hamiltonian was recently extended to include three and four stretching bonds (Law and Duncan, 1994). $H_s + H_b + H_f + H_{sb}$ is an effective Hamiltonian given by Baggott (1988).

We can now calculate the Hamiltonian matrix elements in the symmetrized bases, then fit the experimental data of SO_2 (Guelachvili *et al.*, 1988; Brand *et al.*, 1973) by a least squares optimization to determine the 17 parameters in the model (Fit 1). As a check we also determine the 15 parameters in the corresponding undeformed model (Fit 2). The observed vibrational levels with their normal mode assignments (Guelachvili *et al.*, 1988; Brand *et al.*, 1973) and the calculated residuals (calculated – observed) are presented in Table I, where our results are compared with those of the vibron model (Iachello and Oss, 1990) and the undeformed model. The parameters obtained are given in the last two columns of the table. The last line of the table gives their standard deviations (SD).

The q -deformed boson-realization model and the corresponding undeformed model give the vibrational energy levels of sulfur dioxide with the standard deviations 2.36 and 2.47 cm^{-1} , respectively. Calculation shows that the predicted levels are very sensitive to q_s and q_b and that the best fit requires that those two parameters approximate to one. The two parameters q_s and q_b have an effect on the coupling constants (see table), but the q -deformed

Table I. Observed Data, Residuals, and Parameters^a

ν_1	ν_2	ν_3	Observed	IO ^b	Fit 1	Fit 2	Parameters
0	1	0	517.87	0.13	-1.16	-1.50	Fit 1
1	0	0	1151.71	-4.21	-2.01	-2.01	ω_s 1274.020
0	0	1	1362.06	0.54	0.93	1.26	x_s -9.493
0	2	0	1035.13	0.17	-3.17	-3.59	ω_b 517.497
1	1	0	1666.33	-1.63	0.61	0.52	x_b -0.393
0	1	1	1875.80	0.20	-0.27	-0.54	λ_{s1} -110.170
2	0	0	2295.81	-7.71	-2.80	-2.84	λ_{s2} 5.497
1	0	1	2499.87	0.53	-0.42	-0.51	λ_{s3} -2.810
0	0	2	2715.46	-1.96	-1.90	-1.42	λ_{s4} 1.100
0	3	0	1551.1	0.80	-3.25	-3.44	λ_f -8.729
1	2	0	2179.51	1.79	1.44	1.21	λ_{sb1} 0.739
0	2	1	2388.92	-0.02	-0.46	-0.89	λ_{sb2} -3.425
2	1	0	2807.19	-2.69	0.92	1.20	λ_{fsb1} 1.462
1	1	1	3010.32	2.88	-0.51	-1.15	λ_{fsb2} 2.871
0	1	2	3222.25	0.35	-0.30	-0.38	λ_{fsb3} -1.175
3	0	0	3431.19	-9.39	-0.96	-1.18	λ_{fsb4} 1.310
2	0	1	3629.61	0.69	-0.30	-0.71	q_s 1.0016
1	0	2	3837.06	4.64	1.73	1.78	q_b 1.0039
0	0	3	4054.26	-1.46	-2.56	-2.12	
0	4	0	2066.87	0.73	-1.17	-0.84	Fit 2
0	2	2	3730.9	0.00	0.58	0.42	ω_s 1271.910
3	1	0	3939.9	-2.40	1.56	2.12	x_s -8.368
4	0	0	4560.1	-2.60	1.73	1.15	ω_b 514.895
3	0	1	4751.23	3.97	1.71	1.18	x_b 0.737
1	0	3	5165.64	5.76	2.15	2.36	λ_{s1} -110.308
0	5	0	2582.3	-0.10	4.13	5.24	λ_{s2} 4.197
0	3	2	4241.5	-3.10	0.66	0.64	λ_{s3} -2.556
3	2	0	4446.9	5.60	2.12	2.63	λ_{s4} 1.082
1	2	2	4848.14	9.66	4.08	4.86	λ_f -8.780
4	1	0	5070.3	-6.70	-1.71	-1.20	λ_{sb1} 1.001
4	0	1	5872.1	8.80	-1.35	-1.72	λ_{sb2} -3.430
1	0	4	6489.2	0.30	-2.72	-2.52	λ_{fsb1} -1.655
0	0	5	6689.4	7.60	1.20	0.99	λ_{fsb2} 4.487
2	4	0	4342.7	6.40	-2.25	-2.35	λ_{fsb3} -0.098
3	3	0	4958.0	8.50	-1.58	-1.53	λ_{fsb4} 1.331
5	1	0	6190.7	-7.90	0.43	0.36	
4	1	1	6389.7	-9.30	-1.87	-2.69	
0	5	2	5261.9	-11.60	0.65	0.37	
3	4	0	5465.6	13.90	1.34	0.61	
0	5	3	6564.7	0.80	-0.70	-0.02	
3	4	1	6800.5	-6.60	-0.50	-0.58	
SD				6.10	2.36	2.47	

^a In cm^{-1} , except for q_s and q_b .

^b IO, Iachello and Oss (1990).

model gives a little improvement in the standard deviation. The *q*-deformed model may be more important for higher excited states and can be applied to other polyatomic molecules (Hou *et al.*, 1997). We will do further research on it.

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REFERENCES

- Alvarez, R. N., Bonatsos, D., and Smirnov, Y. F. (1994). *Physical Review A*, **50**, 1088.
- Arik, M., and Coon, D. D. (1976). *Journal of Mathematical Physics*, **17**, 524.
- Baggott, J. E. (1988). *Molecular Physics*, **65**, 739.
- Bonatsos, D., and Daskaloyannis, C. (1993). *Physical Review A*, **48**, 3611.
- Bonatsos, D., Paychev, P. P., Roussev, P. R., and Smirnov, Y. F. (1990). *Chemical Physics Letters*, **178**, 221.
- Bonatsos, D., Daskaloyannis, C., and Kokkotas, K. (1992). *Physical Review A*, **45**, R6153.
- Brand, J. C. D., Humphrey, D. R., Douglas, A. E., and Zanon, I. (1973). *Canadian Journal of Physics*, **51**, 530.
- Chang, Z. (1995). *Physics Reports*, **262**, 137.
- Gupta, R. K., and Cooper, I. L. (1995). *Journal of Chemical Physics*, **102**, 3123.
- Guelachvili, G., Naumenko, O. V., and Ulenikov, O. N. (1988). *Journal of Molecular Spectroscopy*, **131**, 400.
- Hou, X. W., Xie, M., and Ma, Z. Q. (1997). *Physical Review A*, in press.
- Iachello, F., and Oss, S. (1990). *Journal of Molecular Spectroscopy*, **142**, 85.
- Iachello, F., and Oss, S. (1991). *Physical Review Letters*, **66**, 2976.
- Kellman, M. E. (1985). *Journal of Chemical Physics*, **83**, 3843.
- Law, M. M., and Duncan, J. L. (1994). *Molecular Physics*, **83**, 757.
- Ma, Z. Q., Hou, X. W., and Xie, M. (1996). *Physical Review A*, **53**, 2173.
- Xie, M., Hou, X. W., and Ma, Z. Q. (1996). *Chemical Physics Letters*, **262**, 1.