PHYSICAL REVIEW A VOLUME 55, NUMBER 5 MAY 1997

Boson-realization model applied to highly excited vibrations of H_2O

Xi-Wen Hou*
Institute of High Energy Physics, P.O. Box 918(4), Beijing 100039, China
and Department of Physics, University of Three Gorges, Yichang 443000, People's Republic of China

Mi Xie
Graduate School, Chinese Academy of Sciences, Beijing 100039, People's Republic of China

Zhong-Qi Ma
China Center of Advanced Science and Technology (World Laboratory), P.O. Box 8730, Beijing 100080, China
and Institute of High Energy Physics, P.O. Box 918(4), Beijing 100039, People's Republic of China

(Received 7 October 1996)

A boson-realization model and a corresponding q-deformed model are proposed for the vibrations of bent triatomic molecules, where Fermi resonances between stretching and bending vibrations are taken into account. The two models are applied to fit the vibrational energy levels of H_2O up to 22 000 cm^{-1} with the standard deviations 8.198 and 7.157 cm^{-1}, respectively. [S1050-2947(97)03204-6]

PACS number(s): 33.20.Tp

I. INTRODUCTION

The development and refinement of experimental techniques in high-resolution spectroscopy has motivated the progress of theoretical models to interpret and guide such measurements. An algebraic approach [1] was given by Iachello and Levine in terms of the vibron model, where the rotation and vibration of diatomic molecules was described by a U(4) algebra. Later on the model was extended in a natural way to polyatomic molecules by introducing a U(4) algebra for each bond [2], which had the advantage that rotations and vibrations were treated simultaneously [3]. As an alternative scheme, Bijker, Dieperink, and Leviatan proposed another algebraic model [4], in which the relevant point-group symmetry was taken into account exactly and all vibrations and rotations were contained in a single algebraic framework. Iachello and Oss presented an SU(2) algebraic model, which was particularly well suited for dealing with the stretching vibrations of polyatomic molecules such as the octahedral and benzenlike systems [5].

Recently, an important step in the development of algebraic model was to incorporate the bending modes by Iachello and Oss [6,7]. Lemus and co-workers in their recent papers [8–11] proposed a symmetry-adapted algebraic model, where the stretching and the bending vibrations were described in terms of U(2) algebra and products thereof.

On the other hand, U(4) and SU(2) algebraic models were modified by the corresponding quantum algebras [12–14]. They were successfully used for describing the vibrational and rotational spectra of diatomic molecules. Bonatsos and Daskaloyannis [15] gave a q-deformed formalism of Iachello and Oss's SU(2) algebraic model. Other quantum algebraic models [16] were also used for analyzing the rotations and vibrations of diatomic molecules. Recently, we studied the complete vibrations of methane in terms of q-deformed harmonic oscillators instead of the Morse ones [17].

We here are going to extend an algebraic model, called the boson-realization model [18], for bent triatomic molecules, and subsequently restudy it by a q-deformed harmonic-oscillator algebra, where Fermi resonances between the stretching and bending vibrations are considered. In Sec. III we present results calculated by the two models for highly excited vibrational states of H_2O. The conclusion and some discussions are given Sec. IV.

II. HAMILTONIAN

Our attention is paid to the vibrations of bent molecules X_2Y such as H_2O,D_2O, and H_2S, where Fermi resonances between the stretching and bending vibrational states are taken into account. In the normal-mode model, Fermi resonances were treated as perturbative corrections [19], while they were described by the nondiagonal matrix elements of Majorana operators in U(4) algebraic model [20]. In addition, Fermi resonances play an important role in the mechanism of intramolecular vibrational energy redistribution [21,22].

A. Boson-realization model

We introduce three sets of bosonic operators, $a_i^\dagger$ (a_i) ($1\leqslant i\leqslant 2$) and $a_3^\dagger$ (a_3), to describe the stretching and the bending modes of X_2Y, respectively. N_i ($1\leqslant i\leqslant 3$) denotes the phonon number. Those operators satisfy the well-known relations

$$[a_i,a_j^\dagger]=\delta_{ij},\quad [a_i,a_j]=0,\quad [a_i^\dagger,a_j^\dagger]=0. \qquad (2.1)$$

Due to Fermi resonances, we take $2N_1+2N_2+N_3$ as a pre-

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*Electronic address: HOUXW@BEPC3.IHEP.AC.CN

TABLE I. Observed and calculated vibrational levels of H_2O (cm^{-1}).

$E(o)$ [27]	$E(o)-E(c)^a$	$E(o)-E(c)^b$	$E(o)-E(c)^A$	$E(o)-E(c)^B$
1594.7498	0.416	0.061	−2.668	−5.755
3151.63	0.405	0.038	0.016	−6.664
3657.053	0.541	−0.068	3.549	4.754
4666.793	0.934	−0.197	5.464	−3.883
5234.977	0.651	0.311	1.684	3.444
6134.03	0.123	0.769	9.088	−0.045
6775.1	0.028	0.166	1.817	2.390
7201.54	−1.175	−1.303	1.302	1.894
7445.07	0.087	0.655	3.063	4.330
7552	12.162	15.177	11.254	7.363
8273.976	0.676	0.158	0.594	−0.377
8761.582	−1.349	−0.555	0.248	3.898
8890	26.747	38.455	−17.089	−8.597
9000.136	−2.062	0.544	−5.600	−3.665
10 284.367	−1.446	−0.554	−0.405	2.570
10 524.3	−1.368	2.970	−0.950	−0.096
10 599.686	−3.149	−0.587	−3.117	−5.595
10 868.876	−0.523	0.006	5.583	3.343
12 139.2	−5.341	0.071	−6.313	−3.006
12 407.64	−0.864	0.739	3.124	4.746
13 448	−5.670	−3.357	7.777	10.443
13 642.202	−5.630	0.132	−7.521	−3.883
13 828.277	−1.520	5.470	2.052	−5.174
13 910.896	−0.918	0.521	6.188	3.451
14 221.161	−2.442	−0.943	−1.522	−2.677
14 536.87	−4.526	−2.052	9.844	5.066
15 107	−2.763	0.642	−14.579	−14.369
15 344.503	−5.757	4.649	12.518	6.455
15 742.795	−1.416	−0.101	0.179	5.217
16 825.23	−0.925	10.092	−16.629	−17.867
16 898.4	−1.198	16.063	1.469	−4.172
3755.93	−0.021	0.078	0.170	1.698
5331.269	−0.829	−0.085	−5.434	−5.084
6871.51	−2.005	−0.121	−3.398	−4.587
7249.81	−1.173	−0.472	2.611	0.497
8373.853	−1.842	−0.295	4.051	2.299
8807	−2.654	−0.159	−1.858	−1.405
9833.584	0.936	0.580	13.643	14.326
10 328.731	−3.744	−0.236	−0.616	0.020
10 613.355	−2.304	0.618	0.766	−4.272
11 032.406	−1.758	−0.059	5.575	4.204
11 813.19	−2.358	−0.063	2.636	2.347
12 151.26	−5.347	0.926	−3.666	−2.754
12 565	−2.117	−0.116	−9.461	−7.489
13 256	3.384	2.570	4.292	4.723
13 652.656	−6.150	0.853	−3.450	−1.393
13 830.938	−1.181	6.227	0.384	−6.878
14 066.194	−9.876	−0.320	−9.806	−8.253
14 318.813	−2.772	0.928	6.331	0.389
14 640	9.654	5.959	−10.977	−4.945
15 119.029	−3.650	1.366	−3.536	−4.286
15 347.956	−7.428	5.774	−4.276	−2.242
15 832.765	−6.438	1.103	−7.239	−3.063
16 821.635	−2.318	8.231	−2.039	0.760
16 898.842	−0.827	16.413	3.234	−2.383

TABLE I. (*Continued*).

$E(o)$ [27]	$E(o)-E(c)^a$	$E(o)-E(c)^b$	$E(o)-E(c)^A$	$E(o)-E(c)^B$
17 312.539	−7.901	0.476	1.834	0.287
17 495.528	−1.609	5.342	0.756	−2.432
18 265.82	4.781	13.278	−3.654	−3.494
18 393.314	−11.627	13.422	−1.400	5.523
18 989.961	−6.568	4.109	−12.986	−0.096
19 720	21.947	15.823	−0.801	−3.711
19 781.105	23.714	39.891	14.596	14.178
20 543.137	0.796	13.761	−7.555	1.336
21 221.828	15.912	36.137	−6.455	−5.684
SD	9.176	11.121	8.198	7.157
17 227.7	1.500	0.207	11.514	3.867
17 458.354	−2.622	1.984	0.824	−2.854
17 748.073	−6.577	−1.579	−0.279	−2.523
18 320	47.911	25.860	25.584	23.576
18 392.974	−11.102	13.701	−1.070	5.547
21 221.569	16.595	36.354	−5.258	−5.475

served quantity and the total number of phonons. This kind of preserved quantity has been recently used for describing the vibrations of C_{3v} symmetric molecules [23,24]. Neglecting the mixture of the states with different total number of phonons, and assuming interactions up to five orders, we can express the Hamiltonian in terms of the boson operators as

$$\begin{aligned}H=\sum_{i=1}^{2}\ &\omega_s a_i^\dagger a_i(1+x_s a_i a_i^\dagger)+\omega_b a_3^\dagger a_3(1+x_b a_3 a_3^\dagger)+\lambda_1(a_1^\dagger a_2+a_2^\dagger a_1)+\lambda_2(a_1^\dagger a_1 a_2^\dagger a_2)+\lambda_3(a_1^\dagger a_1^\dagger a_2 a_2+\text{H.c.})\\ &+\lambda_4\{(a_1^\dagger a_2+a_2^\dagger a_1)(a_1^\dagger a_1+a_2^\dagger a_2)+\text{H.c.}\}+\lambda_5(a_1^\dagger a_2+a_2^\dagger a_1)a_3^\dagger a_3+\lambda_6(a_1^\dagger a_1+a_2^\dagger a_2)a_3^\dagger a_3+\lambda_7\{(a_1^\dagger+a_2^\dagger)a_3 a_3+\text{H.c.}\}\\ &+\lambda_8\{a_1^\dagger a_2^\dagger(a_1+a_2)a_3 a_3+\text{H.c.}\}+\lambda_9\{(a_1^\dagger a_1^\dagger a_1+a_2^\dagger a_2^\dagger a_2)a_3 a_3+\text{H.c.}\}+\lambda_{10}\{(a_1^\dagger a_1^\dagger a_2+a_2^\dagger a_2^\dagger a_1)a_3 a_3+\text{H.c.}\}\\ &+\lambda_{11}\{(a_1^\dagger+a_2^\dagger)a_3^\dagger a_3 a_3 a_3+\text{H.c.}\},\end{aligned}\tag{2.2}$$

where ω and x are used for comparing them with the constants in the Morse potential, and their footnotes s and b remind us of the stretching and bending modes. $\lambda_i(1\leqslant i\leqslant 11)$ are the coupling constants. The term with λ_7 describes the Fermi resonances between the stretching and the bending vibrations. The last four terms in Eq. (2) are the fifth-order interactions caused by Fermi resonances.

B. *q*-deformed boson-realization model

The generalized deformed oscillator is defined as the algebra generated by the operators $\{1,a,a^\dagger,N\}$ and the structure function $[n]$, satisfying the relations [25]

$$[a,N]=a,\quad [a^\dagger,N]=-a^\dagger,$$

$$a^\dagger a=[N],\quad aa^\dagger=[N+1],\tag{2.3}$$

where $[n]$ is a positive analytic function with $[0]=0$, and N is the number operator. The deformed algebra possesses a Fock space [25] of eigenvectors $|n\rangle$ of the number operator N:

$$N|n\rangle=n|n\rangle,\quad \langle n|m\rangle=\delta_{nm}.\tag{2.4}$$

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

$$|n\rangle=([n]!)^{-1/2}(a^\dagger)^n|0\rangle,\quad [n]!=\sum_{k=1}^{n}[k].\tag{2.5}$$

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

$$a|n\rangle=[n]^{1/2}|n-1\rangle,\quad a^\dagger|n\rangle=[n+1]^{1/2}|n+1\rangle.\tag{2.6}$$

Now we take those q-deformed operators instead of the undeformed ones introduced in Sec. II A. Denote the structure function $[n]_s$ for the stretching modes, and $[n]_b$ for the bending modes. Each set of q-deformed operators satisfies the q-deformed oscillator algebraic relation (3).

Various schemes of deformed oscillator algebras with different structure functions are equivalent from the algebraic viewpoint [25]. For convenience, we choose the first scheme [26], where

$$[n]_s=(q_s^n-1)/(q_s-1), \quad [n]_b=(q_b^n-1)/(q_b-1). \tag{2.7}$$

It is obvious that $[n]_s$ is real if q_s is real. For a positive integer $n, [n]_s<n$ if $0<q_s<1$, and $[n]_s>n$ if $1<q_s$; $[n]_b$ is the same.

We take the same formalism of Hamiltonian Eq. (2) for the q-deformed boson-realization model. It is worthwhile to point out that all operators in this part are q-deformed ones, which are characterized by two different parameters q_s and q_b.

III. APPLICATION TO THE VIBRATIONS OF H_2O

The water molecule is very important not only in human life but also in scientific research where a great deal of attention has been paid to it. Its highly excited vibrational states up to 22 000 cm^{-1} have recently been measured by Rothman *et al.* [27]. Halonen and Carrington proposed a simple vibrational curvilinear internal coordinate Hamiltonian [28] for its vibrational levels up to 18 500 cm^{-1}. The same levels were studied by the U(4) algebraic model [20]. Its vibrations up to 22 000 cm^{-1} were analyzed by the potential-energy surface from *ab initio* calculation [29]. Owing to much research and many experiments on the water molecule, it provides a good testing ground for different models.

We can now calculate the Hamiltonian matrix elements on symmetrized bases, which are the simplest examples of bases [30] for polyatomic molecules, then fit the experimental data by a least-squares optimization to determine the 15 parameters in the boson-realization model (fit A) and the 17 parameters in the corresponding q-deformed model (fit B), respectively. The observed and calculated vibrational levels are presented in Table I, where our results are also compared with those of recent studies. The parameters obtained are given in Table II.

The experimental energies $E(o)$ in cm^{-1} given in Ref. [27] are listed in the first column of Table I. $E(o)-E(c)$ are the differences between the observed data and the calculated values. The energies $E(c)^a$ and $E(c)^b$ are calculated by Xie and Yan [29] using the 17- and 26-parameter potential energy surfaces of Refs. [31] and [32] with the standard deviations (SD) 9.176 and 11.121 cm^{-1}, and the maximum differences 47.911 and 39.891 cm^{-1}, respectively. The results calculated in A and B of the present paper are listed in the last two columns.

IV. CONCLUSION AND DISCUSSION

We have presented a boson-realization model with 15 parameters and a corresponding q-deformed model with 17 parameters for the bent triatomic molecules, where Fermi resonances play a key role in coupling the stretching and bending vibrational states. The two models were applied to the highly excited vibrational band origins of the water molecule with standard deviations 8.198 and 7.157 cm^{-1}, and the maximum differences $[E(o)-E(c)]$ 25.584 and 23.576 cm^{-1}, respectively.

TABLE II. Parameters obtained by the least-squares fitting (cm^{-1} except for q_s and q_b).

	Fit A	Fit B		Fit A	Fit B
ω_s	3866.620	3875.780	λ_6	−18.183	−21.237
x_s	−81.119	−86.196	λ_7	7.918	7.705
ω_b	1640.140	1651.370	λ_8	−7.399	−0.421
x_b	−21.361	−25.359	λ_9	−3.719	−3.889
λ_1	−55.247	−54.774	λ_{10}	2.959	1.912
λ_2	−12.840	−12.047	λ_{11}	3.526	4.624
λ_3	−0.329	−0.907	q_s		1.0042
λ_4	1.935	1.783	q_b		1.0058
λ_5	−1.707	−2.853			

The q-deformed model introducing the additional two parameters q_s and q_b gives a slight improvement in the standard deviation, but the two parameters have an effect on the coupling constants (see Table II). Calculations show that the predicted energy levels are very sensitive to q_s and q_b, and that the best fit requires those two parameters to approximate to one. This suggests that both boson operators and q-deformed ones are suitable for describing the vibrations of H_2O. We suppose that the q-deformed model may be more suitable for the higher excited vibrational states of polyatomic molecules. The present two models with fewer parameters may be too simple to include higher-order interactions; therefore, the calculated results for H_2O are not so good as those of Ref. [29], where 24 parameters were used.

In principle, the present model can be applied to the effects of isotopic substitution as well as the vibrations of other polyatomic molecules. Unfortunately, the observed data for D_2O and HDO are too few (less than the number of the parameters) to fit our model. We are looking forward to seeing more data for these.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China and Grant No. LWTZ-1298 of the Chinese Academy of Sciences.

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