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Algebraic Model for Stretching and Bending Vibrations of Bent Triatomic Molecules

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An SU(2) algebraic model is proposed for vibrational spectra of bent triatomic molecules, where Fermi resonances between the stretching and the bending modes are considered. As an example, the model is applied to the 142 vibrational energy levels below 9000 cm^{-1} in the electronic ground state of nitrogen dioxide.

Algebraic methods are now well-established approaches to studying the rotation-vibrational spectra of molecules (Iachello and Levine, 1995). The first step toward those methods was due to Iachello and Levine (1982) through the so-called vibron model, where the rovibronic spectra of diatomic molecules can be described by the U(4) algebra. Later the model was extended in a natural way to polyatomic molecules by introducing a U(4) algebra for each bond. The U(4) model has the two advantages (1) rotations and vibrations are treated simultaneously, and (2) Fermi resonances are described by the nondiagonal matrix elements of Majorana operators, but it becomes quite complex when the number of atoms in molecules is larger than four. By separating the vibrational degrees of freedom from the rotational, Van Roosmalen *et al.* (1983) developed an SU(2) algebraic model for the stretching modes in XYX molecules. An improved SU(2) model (Iachello and Oss, 1991) was particularly well suited for dealing with the stretching vibrations of polyatomic molecules. This model has been extended for both the stretching and the bending modes in X_3 molecules (Frank *et al.*, 1996). As alternative schemes, other Lie algebraic models (Bijker *et al.*, 1995; Leroy and Boujut, 1997) have been presented for molecular spectroscopy. However, they are more complex than the SU(2) model. In a different way, Ma *et al.* (1996),

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using a set of bosonic operators to describe the motion of each bond in polyatomic molecules, have recently proposed another algebraic model, where the interactions between the stretch and the bend are described by a quadratic term or possible Fermi resonance terms (Hou *et al.*, 1997a).

Although Lie algebraic models have been successful for many molecules, they have not yet dealt with the vibrations in polyatomic molecules where Fermi resonances between the stretch and the bend cannot be neglected, especially when the number of atoms in the considered molecule becomes larger than four. Very recently, this case has been studied in terms of boson-realization models (Hou *et al.*, 1998a) as well as in terms of simple Fermi resonance-local mode models for bent triatomic (Halonen and Carring, 1988) and pyramidal XY_3 molecules (Halonen, 1997), where vibrational Hamiltonians are expressed in terms of curvilinear internal valence coordinates, due to Fermi resonances playing an important role in the mechanism of intramolecular vibrational energy redistribution (Wu, 1994). In Lie algebraic models, the SU(2) model is simple and has been extensively used for the description of molecular vibrations (Cooper and Gupta, 1997; Ping and Chen, 1997). Previous studies (Frank *et al.*, 1996; Hou and Ma, 1998; Hou *et al.*, 1998b) on this model suffer from the neglect of the Fermi resonance interactions. In this paper we will study this case in the scheme of the SU(2) algebraic model, and introduce a Fermi resonance-algebraic model. In this model, the SU(2) algebra is used for describing the vibration of each bond, and the relevant interactions are expressed in terms of the operators of SU(2). Our method is addressed to such bent triatomic molecules as NO_2, SO_2, and H_2O, where Fermi resonances between the stretch and the bend are taken into account. In a limit, the model corresponds to the boson-realization model (Hou *et al.*, 1997b). As an example, it will be applied to the recently observed vibrational spectrum in the electronic ground state of nitrogen dioxide (NO_2). The model can be extended for vibrations of molecules with the symmetry groups C_{3v}, T_d, and so on; corresponding results will be discussed elsewhere.

For a bent triatomic molecule XY_2, we introduce three SU(2) algebras to describe three interactions between atoms: $SU_i(2)$ $(1 \leq i \leq 2)$ for X–Y and $SU_3(2)$ for Y–Y interactions. Each $SU_\alpha(2)$ $(1 \leq \alpha \leq 3)$ is generated by the operators $\{\hat{N}_\alpha, \hat{J}_{+,\alpha}\hat{J}_{-,\alpha}, \hat{J}_{0,\alpha}\}$, satisfying the following commutation relations:

$$\begin{aligned} [\hat{J}_{0,\alpha}, \hat{J}_{\pm,\beta}] &= \pm\, \delta_{\alpha\beta}\hat{J}_{\pm,\alpha}, \qquad & [\hat{J}_{+,\alpha}, \hat{J}_{-,\beta}] &= 2\delta_{\alpha\beta}\hat{J}_{0,\alpha} \\ [\hat{N}_\alpha, \hat{J}_{0,\beta}] &= 0 & [\hat{N}_\alpha, \hat{J}_{\pm,\beta}] &= 0 \end{aligned} \tag{1}$$

where $\hat{N}_\alpha$ is related to the Casimir operator of SO(2):

$$2\hat{J}_{0,\alpha}^2 + \hat{J}_{+,\alpha}\hat{J}_{-,\alpha} + \hat{J}_{-,\alpha}\hat{J}_{+,\alpha} = \hat{N}_\alpha(\hat{N}_\alpha/2 + 1) \tag{2}$$

Denote by v_α the number of quanta in the αth bond. The local basis states for each bond are labeled by the eigenvalues N_α of $\hat{N}_\alpha$ and v_α, and written as $|N_\alpha, v_\alpha\rangle$. The action of $\hat{J}_{\pm,\alpha}$ on the local states is given by

$$\begin{aligned}\hat{J}_{+,\alpha}|N_\alpha,v_\alpha\rangle &= \sqrt{v_\alpha(N_\alpha - v_\alpha + 1)}|N_\alpha, v_\alpha - 1\rangle \\ \hat{J}_{-,\alpha}|N_\alpha,v_\alpha\rangle &= \sqrt{(v_\alpha + 1)(N_\alpha - v_\alpha)}|N_\alpha, v_\alpha + 1\rangle\end{aligned} \tag{3}$$

Those equivalent stretching bonds have the same N_j: $N_1 = N_2 = N_s$, and the N_3 for the bending vibration is denoted by N_b.

Since Fermi resonances play a key role in coupling the stretching and bending vibrations, we take $2v_1 + 2v_2 + v_3$ as the preserved phonon number. The Hamiltonian expressed in terms of the operators $\hat{J}_{\pm,\alpha}$ is given as

$$\begin{aligned} H = {} & \eta_1(\hat{J}_{-,1}\hat{J}_{+,1} + \hat{J}_{-,2}\hat{J}_{+,2})/N_s + \eta_2(\hat{J}_{-,1}\hat{J}_{+,2} + \hat{J}_{-,2}\hat{J}_{+,1})/N_s \\ & + \eta_3\hat{J}_{-,3}\hat{J}_{+,3}/N_b + \eta_4(\hat{J}_{-,1}\hat{J}_{+,1}\hat{J}_{-,1}\hat{J}_{+,1} + \hat{J}_{-,2}\hat{J}_{+,2}\hat{J}_{-,2}\hat{J}_{+,2})/N_s^2 \\ & + \eta_5\hat{J}_{-,3}\hat{J}_{+,3}\hat{J}_{-,3}\hat{J}_{+,3}/N_b^2 + \eta_6\hat{J}_{-,1}\hat{J}_{+,1}\hat{J}_{-,2}\hat{J}_{+,2}/N_s^2 \\ & + \eta_7(\hat{J}_{-,1}\hat{J}_{-,1}\hat{J}_{+,2}\hat{J}_{+,2} + H.c.)/N_s^2 \\ & + \eta_8(\hat{J}_{-,1}\hat{J}_{+,2} + \hat{J}_{-,2}\hat{J}_{+,1})(\hat{J}_{-,1}\hat{J}_{+,1} + \hat{J}_{-,2}\hat{J}_{+,2})/N_s^2 \\ & + \eta_9(\hat{J}_{-,1}\hat{J}_{+,2} + \hat{J}_{-,2}\hat{J}_{+,1})\hat{J}_{-,3}\hat{J}_{+,3}/(N_sN_b) \\ & + \eta_{10}(\hat{J}_{-,1}\hat{J}_{+,1} + \hat{J}_{-,2}\hat{J}_{+,2})\hat{J}_{-,3}\hat{J}_{+,3}/(N_sN_b) \\ & + \eta_{11}\{(\hat{J}_{-,1} + \hat{J}_{-,2})\hat{J}_{+,3}\hat{J}_{+,3} + H.c.\}/(N_sN_b) \\ & + \eta_{12}\{\hat{J}_{-,1}\hat{J}_{-,2}(\hat{J}_{+,1} + \hat{J}_{+,2})\hat{J}_{+,3}\hat{J}_{+,3} + H.c.\}/(N_s^{3/2}N_b) \\ & + \eta_{13}\{(\hat{J}_{-,1}\hat{J}_{-,1}\hat{J}_{+,1} + \hat{J}_{-,2}\hat{J}_{-,2}\hat{J}_{+,2})\hat{J}_{+,3}\hat{J}_{+,3} + H.c.\}/(N_s^{3/2}N_b) \\ & + \eta_{14}\{(\hat{J}_{-,1}\hat{J}_{-,1}\hat{J}_{+,2} + \hat{J}_{-,2}\hat{J}_{-,2}\hat{J}_{+,1})\hat{J}_{+,3}\hat{J}_{+,3} + H.c.\}/(N_s^{3/2}N_b) \\ & + \eta_{15}\{(\hat{J}_{-,1} + \hat{J}_{-,2})\hat{J}_{-,3}\hat{J}_{+,3}\hat{J}_{+,3}\hat{J}_{+,3} + H.c.\}/(N_s^{1/2}N_b^2) \end{aligned} \tag{4}$$

where $\eta_k (1 \leq k \leq 3)$ are harmonic coupling constants, and the others are anharmonic. The term with η_{11} is the Fermi resonance term in the third-order interaction. The last four terms are the fifth-order interactions related to the Fermi resonances.

If one makes the scale transformations

$$a_\alpha \equiv \hat{J}_{+,\alpha}/\sqrt{N_\alpha}, \qquad a_\alpha^\dagger \equiv \hat{J}_{-,\alpha}/\sqrt{N_\alpha} \tag{5}$$

and takes the limits $N_s \to \infty$ and $N_s \to \infty$, equation (4) is nothing but the

Hamiltonian in the boson-realization model (Hou *et al.*, 1997b), and the Hamiltonian for the stretching vibrations of two bonds (Kellman, 1985) can be obtained from Eq. (4) by neglecting the bending vibrations and their interactions.

Now we apply the model to the vibrational spectrum in the electronic ground state of NO_2. The recently observed data for its vibrational spectrum below 9000 cm^{-1} are taken from Delon and Jost (1991). We first calculate the Hamiltonian matrix elements in the symmetrized bases, then fit the experimental data by a least squares optimization to determine the 15 parameters in the model. For comparison, we have made two fits. The model in Fit 1 is taken in the harmonic limit; in Fit 2 we choose the boson numbers $N_s = 75$ and $N_b = 1050$, because the bending vibration is far more harmonic than the stretching vibrations. The observed vibrational energy levels and the calculated differences (calculated $-$ observed) for both Fits 1 and 2 are presented in Table I, where our results are also compared with those calculated by Xie and Yan (1996) from the potential energy function of Tashkun and Jensen (1994). The obtained parameters for two fits are listed in Table II.

The standard deviations (SD) in Fits 1 and 2 are 3.29 and 2.68 cm^{-1}, respectively. Although the Fermi resonance-algebraic model provides a little improvement over the SD obtained in the boson-realization model, more sample calculations are needed to judge which model is better. The SDs indicate that our models can well reproduce the experimental data and can be compared with the results of Xie and Yan (1996), where an *ab initio* calculation was made via the self-consistent field configuration interaction method. This calculation can be successfully applied to small molecules, but quickly becomes a formidable problem in the case of larger molecules due to the size of their configuration spaces. The present calculations for this sample molecule and others (Chen *et al.*, 1996; Frank *et al.*, 1996; Hou *et al.*, 1998a, b) demonstrate that algebraic methods can be used as an effective approach to molecular vibrations with good precision. These methods are particularly useful when describing vibrations of large molecules and for high overtones, especially when no *ab initio* calculations are available.

In summary, we have introduced a Fermi resonance-algebraic model for vibrations of bent triatomic molecules, where Fermi resonances are dominant in coupling the stretching with the bending states. In the limit, the model corresponds to the boson-realization model. These two models have been successfully applied to the 142 vibrational energy levels below 9000 cm^{-1} of nitrogen dioxide in the electronic ground state. Application and extension of the models to large molecules are in progress.

Table I. Observed Vibrational Energy Levels and Calculated Differences[a]

Observed	XY[b]	Fit 1	Fit 2	Observed	XY[b]	Fit 1	Fit 2
749.649	−0.57	0.45	0.94	5224.55	−1.53	−0.55	0.73
1319.794	2.04	2.95	1.38	5298.16	1.69	−0.76	0.77
1498.34	−0.67	0.61	1.54	5377.91	4.07	2.81	2.96
1616.852	3.83	1.34	1.86	5384.41	4.20	0.93	−0.35
2063.118	−0.73	2.79	1.49	5437.54	9.19	−1.94	−2.48
2246.04	−0.70	0.50	1.78	5469.66	14.53	2.61	1.93
2355.151	2.04	1.58	2.16	5568.41	0.30	0.75	−1.40
2627.337	4.74	4.56	2.67	5630.36	1.48	−2.47	−4.06
2805.6	−1.78	2.12	1.20	5701.41	13.60	−2.78	−2.91
2906.074	4.40	0.38	−0.34	5762.23	−0.51	−0.77	−0.08
2993.0	−1.17	−0.15	1.38	5826.29	1.94	−1.11	−1.76
3092.481	1.47	1.45	2.19	5898.94	7.25	0.15	−0.82
3201.433	8.31	2.35	2.60	5930.66	6.33	0.73	0.98
3364.57	0.83	3.76	1.89	5965.61	−1.83	−0.52	0.25
3547.1	−2.00	1.10	0.60	5984.705	18.67	−2.37	−2.34
3637.843	1.51	0.40	−0.54	6030.71	1.68	−1.54	0.21
3738.6	−1.60	−0.72	0.90	6101.80	5.19	1.82	2.23
3829.34	−0.97	0.43	1.42	6112.11	3.29	0.15	−0.93
3922.61	6.81	4.57	3.40	6156.25	6.29	−2.35	−3.19
3929.12	6.42	1.68	1.70	6183.61	15.09	2.83	2.05
4100.58	−0.39	2.77	1.10	6275.98	24.57	1.15	0.35
4179.938	6.29	−0.79	−1.81	6299.70	1.73	0.24	−0.15
4286.82	−1.30	0.49	0.43	6351.40	3.64	−1.28	−2.92
4369.1	−0.21	−0.47	−1.45	6414.16	12.03	−1.85	−2.34
4461.07	9.23	−1.37	−1.69	6475.05	11.46	−0.58	1.99
4482.57	−1.83	−0.97	0.57	6497.60	−0.96	−1.13	−0.19
4564.22	1.50	0.05	1.31	6552.84	2.87	−1.50	−1.87
4652.0	3.46	4.99	3.66	6616.53	7.59	0.19	−0.85
4656.34	5.53	0.10	0.11	6653.54	5.52	−0.44	−0.18
4754.209	15.20	2.56	2.20	6676.86	12.76	−1.91	−1.41
4835.05	−0.08	1.91	0.59	6693.12	20.30	−1.83	−2.15
4905.52	2.93	−1.29	−2.69	6705.23	−2.25	−0.39	−0.36
5025.2	−0.66	−0.13	0.22	6771.44	1.62	−11.86	−9.97
5098.0	1.21	−0.40	−1.26	6823.80	6.18	1.37	2.10
5180.54	7.43	−0.46	−1.20	6837.75	3.34	−0.02	−0.76
5205.81	9.67	2.42	2.81	6872.10	6.93	−1.29	−2.35
6897.37	14.88	1.90	1.22	8093.10	12.33	3.13	3.83
6921.67	21.04	−1.72	−1.03	8110.13	21.10	−4.82	−5.42
6979.21	26.55	1.95	0.88	8120.70	31.29	1.80	4.38
7029.48	0.26	−0.18	−0.06	8174.27	1.77	−2.44	−1.73
7072.23	4.75	−1.30	−2.87	8178.27	31.76	2.05	−0.27
7125.60	12.01	−0.95	−1.69	8218.84	−1.48	−2.56	−0.74
7192.29	27.79	−2.49	−1.50	8264.28	5.18	−0.13	1.36
7193.35	9.02	−2.51	0.27	8284.17	0.21	3.29	0.32
7231.06	−2.10	−0.95	0.11	8299.45	9.19	0.94	−0.30
7277.83	3.20	−1.74	−1.79	8320.00	14.66	0.91	0.89

Table I. Continued

Observed	XY[b]	Fit 1	Fit 2	Observed	XY[b]	Fit 1	Fit 2
7332.45	8.52	0.52	−0.46	8330.35	20.88	1.31	2.73
7374.57	5.30	−1.18	−0.81	8374.58	43.80	4.06	6.52
7386.33	11.33	−0.07	0.56	8382.64	27.55	2.74	1.78
7403.04	19.91	−4.09	−4.61	8441.44	11.50	−7.09	−0.97
7443.09	−2.61	0.17	−0.83	8457.15	43.66	0.31	−0.35
7478.02	33.09	−3.68	−2.96	8482.12	−4.25	2.65	2.67
7492.23	−0.71	−3.61	−1.68	8507.33	6.34	0.93	−0.29
7544.62	6.22	0.72	1.83	8542.25	15.32	3.52	2.04
7562.47	1.81	−0.71	−1.03	8585.54	21.45	7.49	8.51
7587.04	7.72	−0.73	−1.91	8608.92	29.76	−8.97	−6.01
7609.57	14.78	1.19	0.77	8623.34	7.78	−3.93	−0.78
7627.14	20.00	−0.40	0.38	8652.27	31.89	−0.07	2.77
7681.49	27.32	2.41	1.29	8690.72	11.67	0.60	3.28
7730.08	12.53	−6.15	0.11	8721.11	1.61	0.19	0.72
7757.29	−1.50	−0.05	0.56	8758.28	10.45	3.43	2.43
7766.28	30.52	−1.37	−1.98	8797.95	13.76	6.92	6.97
7791.18	15.95	−0.87	−2.29	8809.81	2.98	−0.19	0.68
7834.97	13.38	0.70	−0.24	8817.61	31.06	5.06	8.14
7888.16	20.82	3.85	4.87	8816.65	20.99	−6.26	−6.85
7909.46	8.40	−4.93	−0.67	8868.35	38.50	−0.49	0.57
7903.54	28.46	−7.54	−5.63	8911.29	−2.31	4.75	0.78
7962.27	−3.99	0.08	1.11	8941.28	−1.34	−5.57	−3.43
8000.93	2.65	−1.51	−1.26	8944.50	49.95	−1.89	−0.41
8046.44	9.59	1.42	0.57	8968.55	13.92	16.60	−2.23
8093.61	4.38	0.55	−0.80	8982.08	3.63	−0.90	1.34
				SD	14.28	3.29	2.68

[a] In cm^{-1}.

[b] Xie and Yan (1996).

Table II. Parameters (in cm^{-1}) Obtained in the Two Fits

	Fit 1	Fit 2		Fit 1	Fit 2
η_1	1490.858	1471.623	η_9	2.435	4.318
η_2	−152.870	−147.809	η_{10}	−9.124	−7.672
η_3	750.788	751.482	η_{11}	−2.407	−9.233
η_4	−20.324	−0.712	η_{12}	0.102	0.858
η_5	−0.690	−0.898	η_{13}	1.102	0.609
η_6	0.427	1.246	η_{14}	−0.024	−0.183
η_7	−3.040	−3.282	η_{15}	0.019	0.022
η_8	5.212	4.804			

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