PHYSICAL REVIEW A VOLUME 56, NUMBER 4 OCTOBER 1997

Molecular staggering in AgH and its description in terms of parity-split q rotators

Peter Raychev,[1,*] Jean Maruani,[2,†] and Svetla Drenska[1]
[1] Institute of Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences, 72 Tsarigradsko Chaussee, Sofia 1784, Bulgaria
[2] Laboratoire de Chimie Physique, CNRS and UPMC, 11 rue Pierre et Marie Curie, 75005 Paris, France

(Received 12 February 1997)

It is shown that the $\Delta J=4$ bifurcation effect recently discovered in the superdeformed bands of heavy nuclei also occurs in the rotational bands of diatomic molecules in the form of a $\Delta J=2$ staggering. A possible explanation for this phenomenon assumes a perturbation between rotational levels that can be described in terms of parity-split q-deformed rotators interacting through a q-deformed, J-dependent interaction. The phenomenon is evidenced and the model is illustrated on the rotational bands of AgH. [S1050-2947(97)09810-7]

PACS number(s): 31.10.+z, 33.15.−e

I. INTRODUCTION

It is known that the rotational bands of diatomic molecules [1–3] and those of atomic nuclei [4,5] have many features in common, in spite of the great difference of the excitation energies involved. In the last decade much attention has been paid to the superdeformed nuclear bands [6], which have higher angular momenta and behave closer to the rigid rotator than normal deformed nuclear bands. Since the behavior of some molecular rotational bands is closer to the rigid rotator than that of standard nuclear rotational bands, and since in molecular bands one can discover states with very high values of angular momentum, one can expect that some effects typical of superdeformed nuclear bands can also be found in molecular bands.

A rather surprising feature has been discovered recently [7,8] in superdeformed nuclear bands: sequences of states differing by four units of angular momentum appear displaced relative to each other, the relative shifts being of the order of 10^{-4} the energies separating the band levels. This effect has been called the $\Delta J=4$ bifurcation because the bands seem to split into two sequences with levels differing by four units in J. The quantitative description of this effect is given in what follows.

In nuclear physics the experimentally observed quantities are the γ-ray transition energies between levels differing by two units of angular momentum ($\Delta J=2$) [4]. For these quantities the symbol

$$E_2(J)=E(J+2)-E(J) \tag{1}$$

is used, where $E(J)$ denotes the energy of the level with angular momentum J. The deviation of these transition energies from the rigid rotator behavior can be measured by the quantity [8]

$$\Delta E_2(J)=\tfrac{1}{16}[6E_2(J)-4E_2(J-2)-4E_2(J+2)+E_2(J-4)+E_2(J+4)]. \tag{2}$$

Substituting the rigid rotator expression $E(J)=AJ(J+1)$ into Eq. (1), then Eq. (1) into Eq. (2), one can check that in this case $\Delta E_2(J)$ vanishes: in this sense this quantity expresses the deviation of nuclear spectra from the regular $J(J+1)$ law.

In Fig. 1 there are shown $\Delta J=4$ staggerings for the superdeformed nuclear bands of ^{149}Gd (a) [7] and ^{194}Hg (b) [8]. From the figure it appears that $\Delta E_2(J)$ takes alternating positive and negative signs when J increases by four-unit steps. The magnitude of $\Delta E_2(J)$ is of the order of 10^{-4} that of the γ-ray transition energies. Regarding the physical meaning of such $\Delta J=4$ staggerings some proposals have been made, which involve intricate crossing of nuclear levels [9] or dynamical breaking of nuclear symmetries [10–14], as in quantum bifurcations at diabolic points for spherical-top molecules [15,16]. However, it was recently reported [17] that $\Delta J=4$ bifurcations also occur in the rotational spectra of diatomic molecules such as CrH, CrD, or Cu$_2$, as well as $\Delta J=8$ bifurcations in atomic nuclei and diatomic molecules.

The observation of $\Delta J=4$ and 8 staggerings in both nuclei and molecules suggests that some common and rather general mechanism may exist, which would generate such similar effects in different systems. Even though the excitation energies in nuclear and molecular rotational spectroscopies are very different (about 10^5 eV in nuclei and 10^{-2} eV in molecules), the observed staggerings are of the same order of magnitude ($\approx 10^{-4}$). As the experimental techniques involved are very specific, the occurrence of such similar systematic errors is very unlikely.

The aim of this paper is to give evidence for $\Delta J=2$ staggering in the rotational bands of the AgH molecule [18,19], to make a systematic investigation of this effect in the different rotational bands, and to propose a qualitative description of the staggering phenomenon using q-deformed algebras, as we have done previously [20] for the backbending phenomenon in the same molecule.

II. DERIVATION OF BACKBENDING AND STAGGERING FROM THE TRANSITION ENERGIES

The deviations of rotational spectra from the rigid rotator model can best be demonstrated by investigating the dependence of the effective ‘‘moment of inertia’’ upon the effective ‘‘angular velocity,’’ which may then display ‘‘upbend-

---

[*] Electronic address: raychev@bgcict.acad.bg

[†] Electronic address: maruani@moka.ccr.jussieu.fr

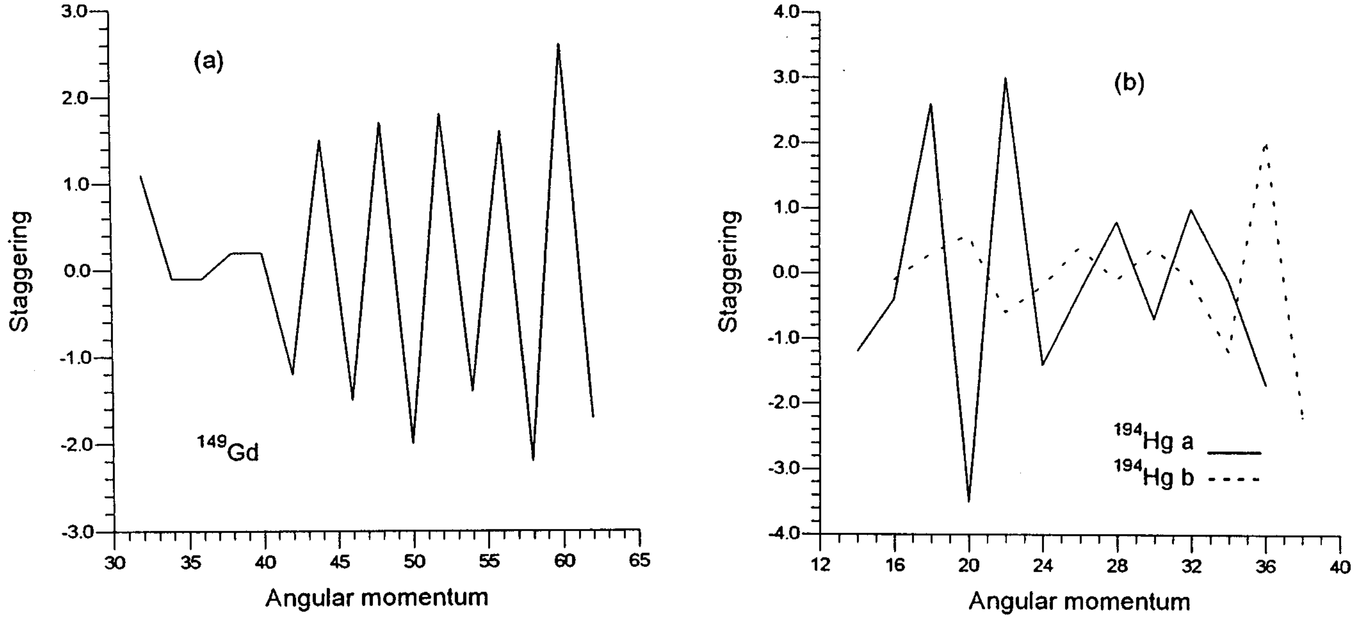

FIG. 1. $\Delta J=4$ staggerings, as defined in Eq. (2), for the superdeformed bands of ^{149}Gd (a) and ^{194}Hg (b) nuclei (adapted from Refs. [7] and [8]).

ing'' and ``backbending'' phenomena. Here we shall briefly recall some of our previous results [20].

The classical expressions for the rotational energy E and angular momentum L of a rotating body are

$$E=\frac{1}{2\mathcal{J}}L^2, \quad L=\mathcal{J}\omega. \tag{3}$$

In quantum mechanics the inertial momentum $\mathcal{J}$ and angular velocity ω are not directly measurable quantities. However, they can be derived from the experimental data by using the relations

$$\frac{dE}{dL}=\frac{L}{\mathcal{J}}=\omega, \quad \frac{dE}{dL^2}=\frac{1}{2\mathcal{J}}. \tag{4}$$

We can calculate $\mathcal{J}$ and ω by replacing dL and dE with the experimentally measured finite differences and using the semiclassical expression $L=\sqrt{J(J+1)}$:

$$\begin{aligned}\Delta E&=E(J)-E(J-1),\\ \Delta L&=L(J)-L(J-1)=\sqrt{J(J+1)}-\sqrt{(J-1)J},\end{aligned} \tag{5}$$

this yielding

$$\frac{dE}{dL}=\omega\rightarrow\omega_{\text{expt}}=\frac{\Delta E}{\Delta L}, \quad \frac{dE}{dL^2}=\frac{1}{2\mathcal{J}}\rightarrow\mathcal{J}_{\text{expt}}=\frac{\Delta L^2}{2\Delta E}. \tag{6}$$

The final result is

$$\begin{aligned}\mathcal{J}_{\text{expt}}&=k_1\,\frac{2(2J-1)}{E(J)-E(J-1)},\\ \omega^2_{\text{expt}}&=k_2\left[\frac{E(J)-E(J-1)}{\sqrt{J(J-1)}-\sqrt{(J-1)J}}\right]^2,\end{aligned} \tag{7}$$

where k_1 and k_2 are factors depending upon the choice of the units. Equations (7) are a parameteric representation of $\mathcal{J}_{\text{expt}}$ as a function of ω^2_{expt}. Typical examples of this functional dependence are given in Fig. 2 (right column), where the deviations of the levels from the $J(J+1)$ law appear more clearly than in the energy diagrams, shown in Fig. 2 (left column). In lower regions the dependence of $\mathcal{J}_{\text{expt}}$ upon ω^2_{expt} resembles the lower part of an S (upbending), whereas in higher regions it resembles the higher part of the S (backbending). It has been shown [20] that upbending can be described by assuming the energy levels distort according to a nonrigid molecule model, whereas backbending stems from independent rotational bands repelling each other due to their interaction at crossing points. In that sense the appearance of backbending is evidence of strongly interacting rotational bands.

While the $\mathcal{J}_{\text{expt}}(\omega^2_{\text{expt}})$ representation of the transition energy E_t upon the quantum number J enhances the manifestation of the spectra irregularities over a large range of rotational states in the form of backbending, successive derivations of E_t with respect to J will enhance its local variations in the form of staggering. By analogy with nuclear staggering, molecular staggering can be defined in the following way. Let us denote by $E'(v,J)$ and $E''(v,J)$ ($J=0,1,2,\ldots$) the rotational levels belonging to rotational bands built up on the vibrational levels with quantum numbers v, with E' and E'' referring to upper and lower electronic states, respectively. By analogy with Eq. (1), we form the differences

$$E_t(v,J)=E(v,J)-E(v,J-1), \tag{8}$$

which correspond to the transition energies within rotational bands [1] (when the vibrational band will be clear from the context the quantum number v will be omitted). Then, by analogy with Eq. (2), we define staggering in molecular bands by the formula

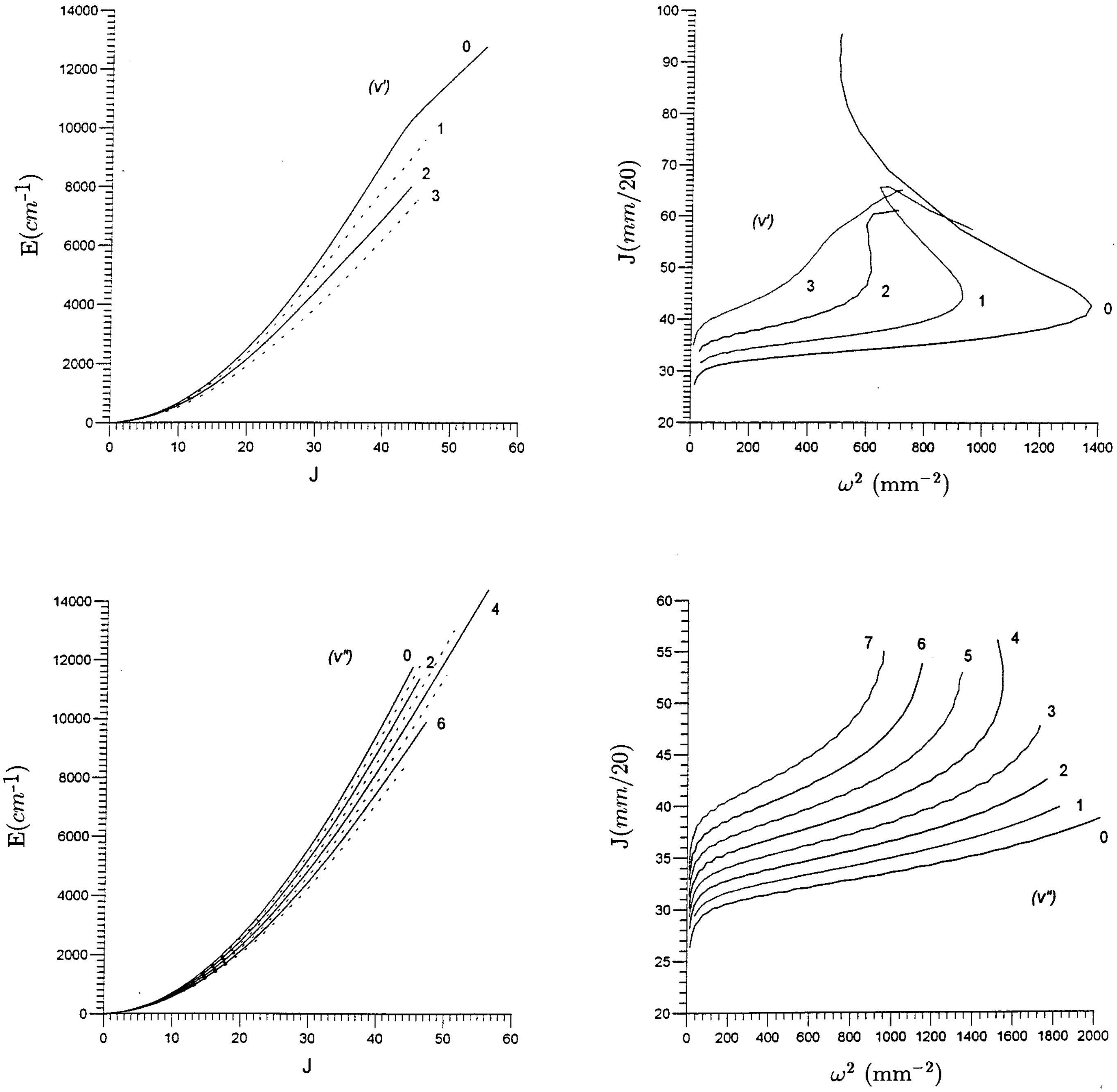

FIG. 2. Energy curves (left) and backbending curves (right) for some of the lower (bottom) and upper (top) rotational bands of the AgH molecule. The level energies and backbending coordinates are derived from transition energies as explained in the text.

$$\Delta E_t(J) = \frac{1}{h^4}\{E_t(J+2h) - 4E_t(J+h) + 6E_t(J) - 4E_t(J-h) + E_t(J-2h)\}. \tag{9}$$

If $h=1,2,4,\ldots$, we speak of $\Delta J = 2,4,8,\ldots$ staggering, respectively. Again it can be checked that for the rigid rotator—$E(J)=AJ(J+1)$—this expression annihilates for every value of h. In this paper we shall be concerned mainly with $\Delta J=2$ staggering $(h=1)$.

It should be pointed out at this stage that $\Delta E_t(J)$ can be considered formally as a fourth-order ''discrete derivative'' of the discrete function $E_t(J)$. More precisely, for every continuous function, $f(x)$, one has the Taylor expansions:

$$f(x \pm h) = f(x) \pm f^{I}(x)h + \tfrac{1}{2}f^{II}(x)h^2 \pm \tfrac{1}{6}f^{III}(x)h^3 + \tfrac{1}{24}f^{IV}(x)h^4 + h^5 O(x),$$

$$f(x \pm 2h) = f(x) \pm 2\, f^{I}(x)h + 2\, f^{II}(x)h^2 \pm \tfrac{4}{3}f^{III}(x)h^3 + \tfrac{2}{3}f^{IV}(x)h^4 + h^5 O(x), \tag{10}$$

where $O(x)$ gathers the terms containing derivatives of $f(x)$ of order higher than 5. Equations (10) yield a system of 4 equations for the derivatives $f^{(k)}(x)$ $(k=1,2,3,4)$. It is easy to see that for $f^{IV}(x)$ one obtains

$$f^{IV}(x)=\frac{1}{h^4}\{f(x+2h)-4f(x+h)+6f(x)-4f(x-h)+f(x-2h)+h^5O(x)\}. \tag{11}$$

When $h\rightarrow 0$, Eq. (11) reduces to Eq. (9). In our case $h=1$ and $\Delta E_t(J)$ differ from the fourth derivative of $E_t(J)$ (considered as a continuous function of J) by $O(J)$. However, expression (9) has the advantage that if $E(J)$ is given the analytic form of a fourth-order Dunham expansion or of a q-rotator model (see Sec. III), one obtains $\Delta E_t(J)\equiv 0$. In this sense, Eq. (9) ''cleans out'' that part of the energy spectrum which can be described by model formulas (including but not only that for the rigid rotator) and stresses any deviations from them.

In order to calculate $\Delta E_t(J)$ from Eqs. (8) and (9), one must know the level energies $E(J)$ of the rotational band under consideration. Unfortunately, in many instances these energies cannot be determined directly, but only in terms of the quantities

$$\begin{aligned} P(J)&=E''(J-1)-E'(J),\\ R(J)&=E''(J+1)-E'(J), \end{aligned} \tag{12}$$

which are related to the transitions between the upper and lower electronic states according to

$$\begin{aligned} D_2E'(J)&=R(J-1)-P(J+1)=E'(J+1)-E'(J-1),\\ D_2E''(J)&\equiv R(J)-P(J)=E''(J+1)-E''(J-1). \end{aligned} \tag{13}$$

The quantities $D_2E'(J)$ and $D_2E''(J)$ are those usually given in experimental papers (e.g., Ref. [18]), and we must determine $E(J)$, $E_t(J)$ and $\Delta E_t(J)$ from them.

Using the generic formula

$$D_2E(J)=E(J+1)-E(J-1), \tag{14}$$

it can be shown that summing up the experimentally determined quantities $D_2E(J)$ with odd J, one obtains

$$\begin{aligned} \sum_{J(\mathrm{odd})=1}^{J_0} D_2E(J)&=[E(2)-E(0)]+[E(4)-E(2)]+\cdots\\ &\quad+[E(J_0+1)-E(J_0-1)]\\ &=E(J_0+1)-E(0)=E(J_0+1) \end{aligned}$$

if one takes $E(0)=0$ as the beginning of the energy scale. Obviously, J_0+1 is even when J_0 is odd. As shown in the resulting formula,

$$E(J_0+1)=\sum_{J(\mathrm{odd})=1}^{J_0} D_2E(J) \quad (J_0=1,3,5,...), \tag{15}$$

the energy levels with *even* $J=J_0+1$ can be obtained by simple summation of $D_2E(J)$ with *odd* J values. Similarly, the energies $E(J)$ with odd (J_0+1) values can be obtained by means of the following formula:

$$E(J_0+1)=\sum_{J(\mathrm{even})=2}^{J_0} D_2E(J)+E(1) \quad (J_0=2,4,6...). \tag{16}$$

As can be seen from Eqs. (15) and (16), the values of $E(J)$ for *even* J can be derived immediately from the experimental data, whereas those for *odd* J will depend upon the choice of $E(1)$. In general, this energy cannot be obtained directly from the experimental data, and we need a model to derive its value.

For all energy levels we could use an analytic expression of the form

$$E(J)=E(J,\alpha_1,\alpha_2,\ldots,\alpha_n), \tag{17}$$

where $\alpha_1,\alpha_2,\ldots,\alpha_n$ are parameters which may be determined by fitting on the states with odd and even J values. After the fitting is achieved one can calculate $E(1)$ using Eq. (17). This may introduce some errors in the values of $E(J)$ with odd J given by Eq. (16) and it is instructive to consider how these errors would affect the values of $\Delta E_t(J)$ given by Eq. (9).

Let us denote the exact values of the level energies of the energy differences (8) and of the energy staggerings Eq. (9) by $E^0(J)$, $E_t^0(J)$, and $\Delta E_t^0(J)$, respectively. If one denotes the error in the determination of $E^0(1)$ by δ,

$$E(1)=E^0(1)+\delta,$$

all $E(J)$ with odd J will be displaced by the same amount, i.e.,

$$E(J)=\begin{cases} E^0(J) & \text{for } J \text{ even}\\ E^0(J)+\delta & \text{for } J \text{ odd}. \end{cases} \tag{18}$$

Then, according to Eq. (8), we have

$$E_t(J)=\begin{cases} E_t^0(J)-\delta & \text{for } J \text{ even}\\ E_t^0(J)+\delta & \text{for } J \text{ odd}, \end{cases} \tag{19}$$

Substituting these values into Eq. (9), we obtain

$$\Delta E_t(J)=\begin{cases} \Delta E_t^0(J)-16\delta & \text{for } J \text{ even}\\ \Delta E_t^0(J)+16\delta & \text{for } J \text{ odd}. \end{cases} \tag{20}$$

This means that calculation errors of ≈ 0.01 will produce false oscillations of $\approx \pm 0.16$ over real staggering. The same holds, of course, for measurement errors. Fortunately, the observed oscillations of $\Delta E_t(J)$ are an order of magnitude larger, meaning the observed staggering cannot be induced solely by errors from the experimental or fitting procedures.

III. EVIDENCE OF BACKBENDING AND $\Delta J=2$ STAGGERING IN THE ROTATIONAL BANDS OF AgH

As a typical example of the irregularities in molecular rotational bands, we shall consider the microwave spectrum of the AgH molecule [1,18]. We shall show there is evidence not only of backbending, but also of $\Delta J=2$ staggering in this molecular spectrum.

The rovibrational spectra of the AgH molecule have been measured with accuracy up to rotational quantum numbers

$J \approx 60$ and vibrational quantum numbers $v \approx 10$ [18]. Irregularities in the rotational term series occur in transitions within the system $A^1\Sigma^+$-$X^1\Sigma^+$, where the lower state (X) is the ground state, with electronic configuration $KLMNspd(5s\sigma)^2$, and the upper state (A) has the electronic configuration $KLMNspd(5s\sigma)(5p\sigma)$ [1,19].

From these spectra it appears that the behavior of the level series deviates from the $J(J+1)$ law (Fig. 2, left column). This is due to the interaction of the excited electronic state labeled $A^1\Sigma^+$ with a higher electronic state, $B^1\Sigma^+$, having the electronic configuration $KLMNsp(d\sigma)(d\pi)^4(d\delta)^4(5s\sigma)^2(5p\sigma)$ [19]. It has also been seen that these deviations are related to the interplay between several rotational terms belonging to different vibrational levels and crossing over one another alternatively.

An interesting manifestation of the irregularities in this molecular spectrum is the backbending effect, which was investigated earlier [20]. This phenomenon clearly demonstrates the deviation of the rotational levels from the $J(J+1)$ law (Fig. 2, right column). However, backbending is a ‘‘gross’’ manifestation of the irregularities, i.e., it can be observed when J changes over a large range of values. Conversely, staggering has a ‘‘fine’’ structure, i.e., it can be observed in regions where J changes by a few units, as can be seen from the wiggles modulating the backbending curves (Fig. 2, right column). This phenomenon was overlooked in the previous investigation [20] where the fits were made on the even states.

It was shown in Sec. III that, in order to determine molecular staggering in a rotational band, it is necessary to derive the energy levels of the band from the experimental data. The crucial point there is to find the value of $E(1)$ occurring in the expression for the odd states, which cannot be derived directly from the transition energies but only by fitting the data with an appropriate model for the rotational energy.

In order to achieve this goal we have used two independent models: a ‘‘standard model’’ (hereafter referred to as SM), based on a limited Dunham expansion (see Sec. V A), and a ‘‘quantum model’’ (hereafter referred to as QM), based on a quantum, algebraic description of the rotational motion (see Sec. V B). These models have been applied to the microwave spectrum of the AgH molecule. We investigated in detail the four rotational bands build on the lower vibrational levels $v''=0,1,2,3$, and the four rotational bands build on the upper vibrational levels $v'=0,1,2,3$. For each of these eight bands we applied both the SM and QM and, in order to determine the parameters of the model, fitted independently the differences $D_2E(J)$ with even and odd J values. Then we calculated $E(1)$ using both the SM and QM with the two sets of parameters obtained from fitting the even and odd $D_2E(J)$. For each of the bands the values of $E(1)$ obtained in these different ways differed by no more than 0.01 cm^{-1}, which is comparable to the reported accuracy of the experimental data. Finally, we used formulas (15) and (16) to calculate the energies of the levels, and Eq. (9) to calculate the energy staggering.

The results are shown on Fig. 3 for the investigated four upper bands and on Fig. 4 for the investigated four lower bands, Figure 5 showing some additional lower bands for comparison. It can be noticed that, contrary to backbending (Fig. 2, right column), which is observed for values of J starting from ≈ 30, staggering is observed for values of J as low as ≈ 5. In spite of their great variety, the patterns shown are clear evidence of $\Delta J=2$ staggering in all the considered rotational bands of the AgH molecule.

All the staggering patterns display an alternation of low and high staggering amplitudes. The large peaks perturbing the right-hand side ($J>40$) of the $v'=0$ and $v'=1$ patterns (Fig. 3) correspond to the rise of backbending (Fig. 2, upper right diagram); the range of other patterns has been reduced in order to avoid these misscaling peaks. For the upper bands (Fig. 3) the envelopes of the staggering patterns have more or less sinusoidal shapes, with maxima occurring at $J \approx 9-13$ and $J \approx 33-37$ (period $\Delta J \approx 24$) for $v'=0,1,2$ and maxima dephased to lower values of J with a period $\Delta J \approx 20$ for $v'=3$. For the lower bands (Figs. 4 and 5) the envelopes of the staggering patterns appear more chaotic, with waves clearly defined in some patterns ($v''=1,2,4,6$) and poorly spaced in other blocks ($v''=0,3,5,7$). For $v''=0,2,4,6$ there appear regions of lower staggering amplitudes at $J \approx 20-24$ and $J \approx 30-34$, whereas for $v''=1,3,5,7$ less pronounced such regions appear at $J \approx 14-18$, 24–30, and 36–40, revealing an overall period about twice smaller than that for the upper bands.

These regularities are a further argument for the reality of staggering in this molecule: they would be very unlikely if the observed oscillations were due solely to the accumulation of (measurement and calculation) errors (see the end of Sec. III). Some other regularities will be revealed by the Fourier analysis of the oscillating patterns (see the end of Sec. VI).

IV. DESCRIPTION OF ROTATIONAL BANDS IN TERMS OF *q*-INTERACTING, *q*-DEFORMED ROTATORS

A. Standard model (SM) for the description of rotational bands

As we recalled above, in order to determine the energy $E(1)$ which enters expression (16) of $E(J)$ for odd J, then that [Eq. (9)] of the (experimental) staggering, we need a (theoretical) model for calculating the levels. In an ideal rotational spectrum, these levels would be described by the formula

$$E(J)=\frac{1}{2\mathcal{J}}J(J+1), \tag{21}$$

where $\mathcal{J}$ is the moment of inertia of the molecule (or nucleus), assumed to be a constant. However, this formula fails to describe the levels with higher values of J, because the centrifugal force then causes the molecule (or nucleus) to distort, and its moment of inertia to increase. The *standard* model for the description of rotational spectra is an expansion of the form [1,2]

$$\begin{aligned}E_v(J)=&B_vJ(J+1)+D_v[J(J+1)]^2+H_v[J(J+1)]^3\\&+J_v[J(J+1]^4+\cdots ,\end{aligned} \tag{22}$$

where v and J are the vibrational and rotational quantum numbers, respectively. It is known empirically that the coefficients $B_v, D_v, H_v, \ldots$ have alternating signs, starting with B_v positive [1]. In addition, D_v is roughly 3–4 orders of magnitude smaller than B_v, and H_v is also 3–4 orders of

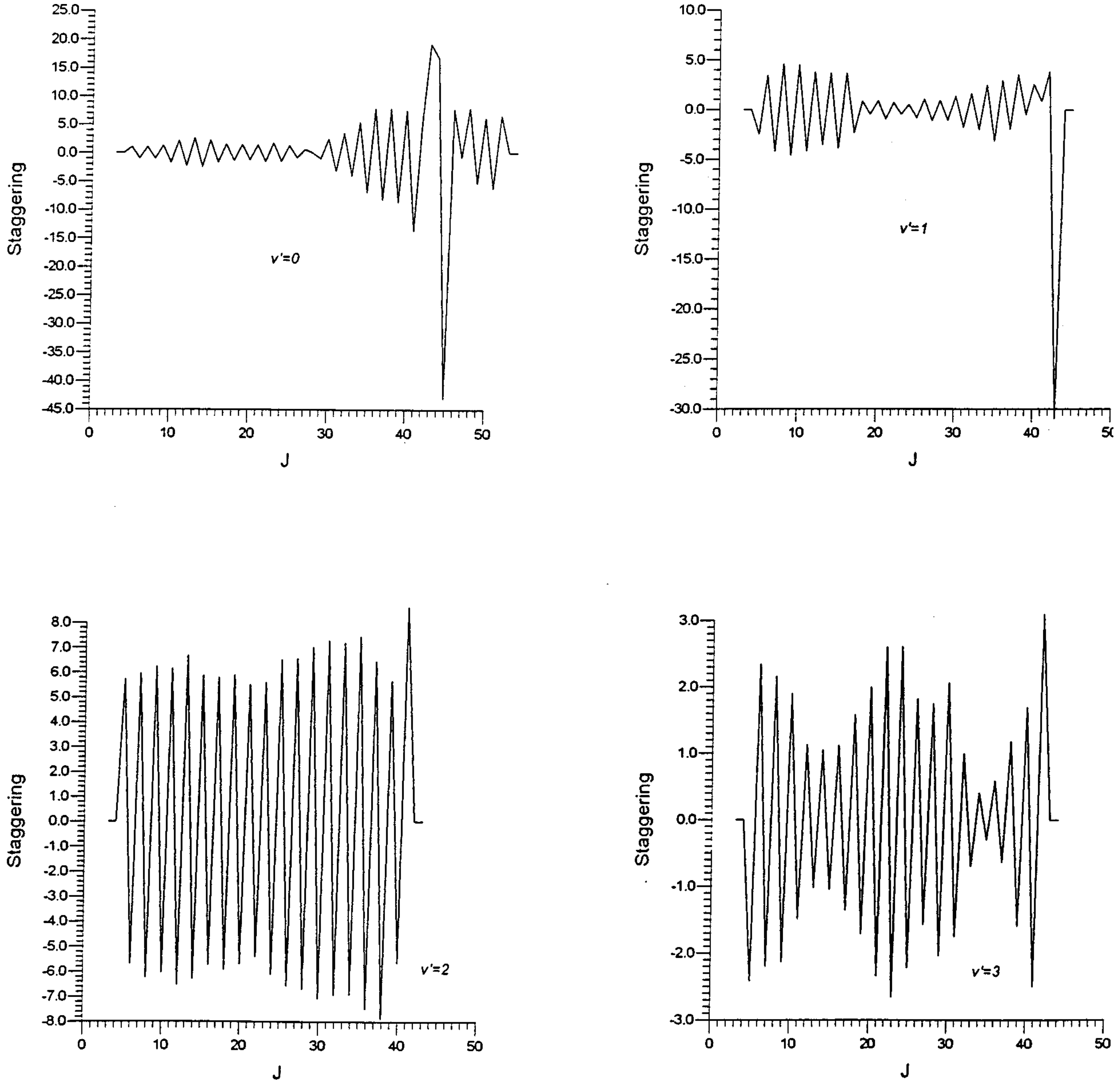

FIG. 3. Staggering $\Delta E_t(J)$, as defined in Eq. (9), for the upper rotational bands $v' = 0,1,2,3$ of the AgH molecule (in cm^{-1}).

magnitude smaller than D_v. More generally, rovibrational spectra of molecules (and nuclei) can be described by a limited Dunham expansion [21]

$$E(v,J)=\sum_i \sum_k Y_{ik}(v+1/2)^i[J(J+1)]^k, \tag{23}$$

where the Y_{ik}'s are numerical coefficients. For molecular systems, the first few terms of this expansion can be obtained by solving the Schrödinger equation for the nuclear motion with some potential such as that proposed by Morse [22]. Even though the Dunham expansion is usually related to the adiabatic approximation, it has been shown [23] to have a more general interpretation in terms of the generator-coordinate method. The connection between the coefficients $B_v, D_v, H_v, \ldots$ of Eq. (17) and those Y_{ik} of Eq. (18) is straightforward.

Both expressions (22) and (23) give a very good description of rotational spectra involving pure anharmonicity, when there is no mutual perturbation of the levels. They can therefore be used for describing known rotational levels and, after fitting the coefficients $B_v, D_v, \ldots$ (or Y_{ik}), for calculating $E(1)$, as explained in Sec. III.

B. Quantum model (QM) for the description of rotational bands

1. *Standard and quantum algebras* su(2) *and* $\mathrm{su}_q(2)$

Along with the standard model (e.g., the Dunham expansion), there is an alternative approach to the description of the vibrational and rotational (molecular and nuclear) spectra involving anharmonicity of the interaction potential, based on what is known as quantum groups (i.e., Hopf algebras). Quantum groups are a powerful branch of modern mathematics which, in the last decade, have found a wide variety

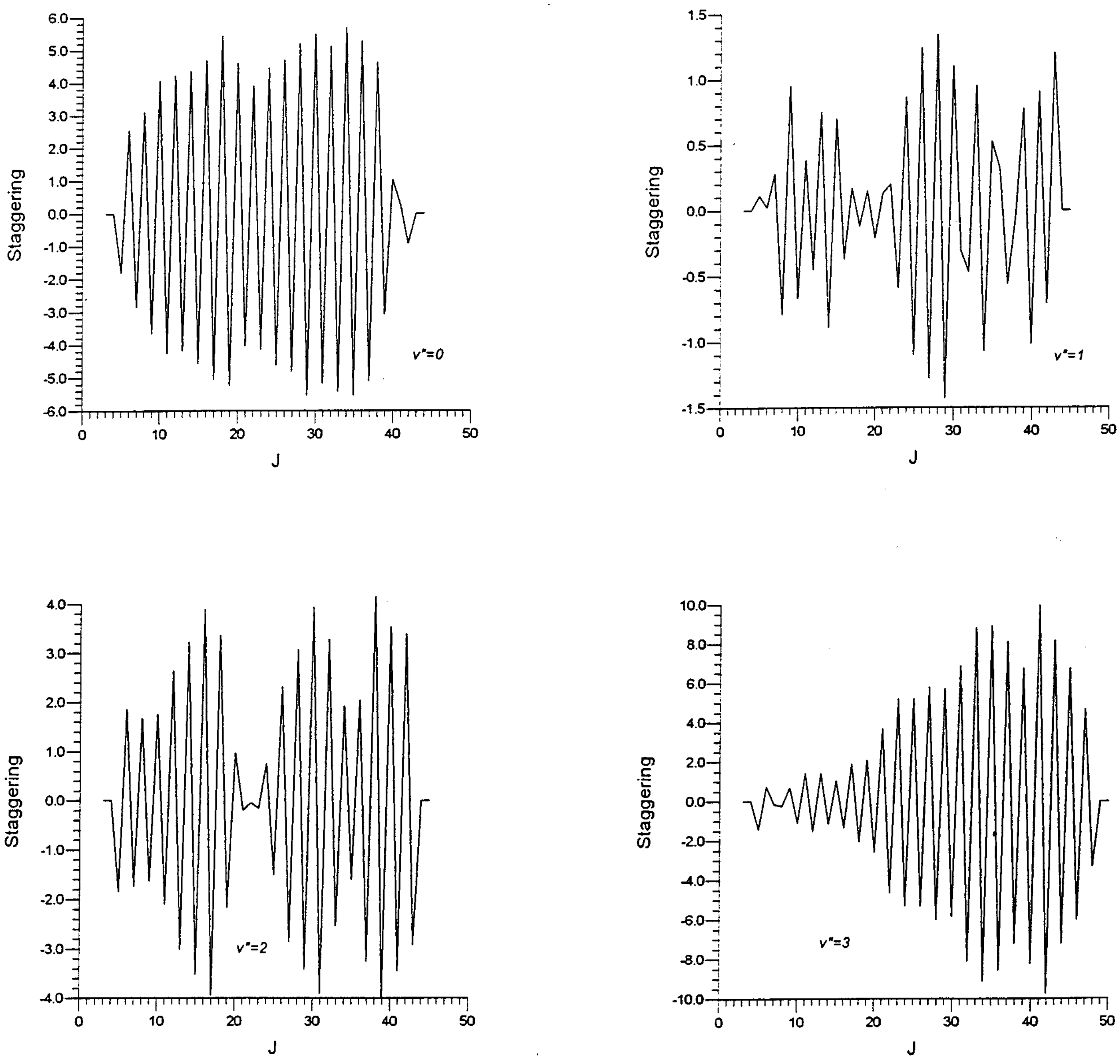

FIG. 4. Staggering $\Delta E_t(J)$, as defined in Eq. (9), for the lower rotational bands $v''=0,1,2,3$ of the AgH molecule (in cm^{-1}).

of applications in the phenomenological description of physical problems, including nuclear and molecular (rotational and vibrational) motions [24–26]. The presentation of quantum groups goes beyond the goal of this paper, and here we shall give only a brief sketch of the physical background and of some elementary techniques which have been used in the description of rotational spectra.

Let us first recall some elementary formulae from the standard theory of angular momentum. The operators L_+, L_0, L_- of angular momentum in quantum mechanics satisfy the commutation relations

$$[L_0, L_\pm] = \pm L_\pm, \quad [L_+, L_-] = 2L_0 \tag{24}$$

and the usual unitary conditions. Operators $L_m(m=+,0,-)$ satisfying the above relations are called generators of the Lie algebra of the su(2) group. From these operators one can build the quadratic linear combination

$$\mathbf{L}^2 = \tfrac{1}{2}(L_+L_- + L_-L_+) + L_0^2 = L_-L_+ + L_0(L_0+1), \tag{25}$$

which describes the square of the angular momentum length. This operator $\mathbf{L}^2$ commutes with all operators L_m:

$$[\mathbf{L}^2, L_m] = 0. \tag{26}$$

In the mathematical literature the bilinear combination $\mathbf{L}^2$ is called the Casimir operator C_2 of the su(2) algebra. We shall also recall that $\mathbf{L}^2$ and L_0 have a common set of eigenvectors $|LM\rangle$, where the quantum number L gives the length of the angular momentum and M gives its projection on the z axis. The operators L_+ and L_- act on the states $|LM\rangle$ by raising or lowering the values of the quantum number M. The vectors $|LM\rangle$ are the basis vectors of the irreducible unitary representations (IUR's) $\mathcal{D}^J$ of the group su(2).

In Sec. IV A we saw that the levels of a rigid rotator can be described by Eq. (21), while for a real rotator a series of

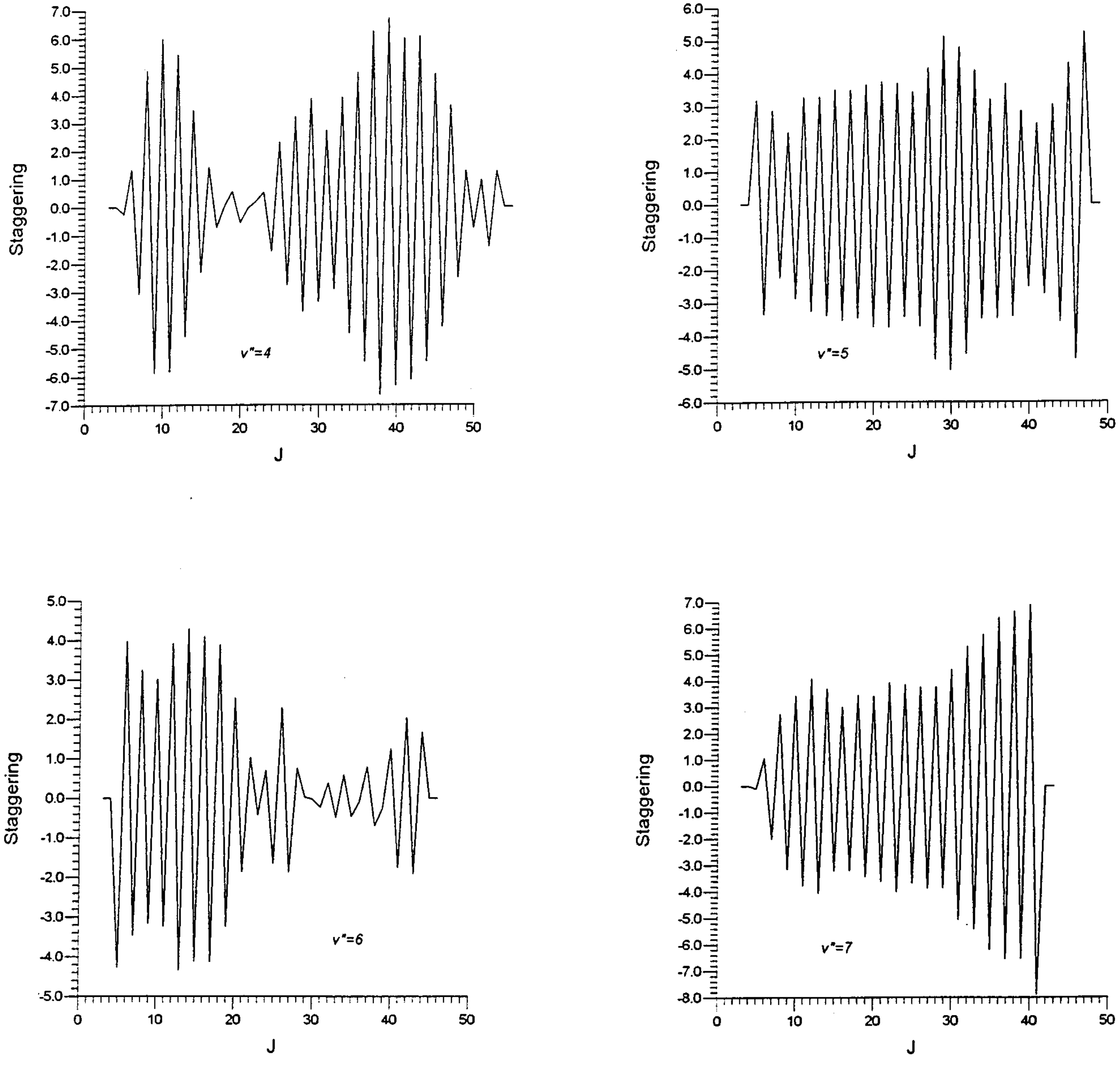

FIG. 5. Staggering $\Delta E_t(J)$, as defined in Eq. (9), for the lower rotational bands $\nu''=4,5,6,7$ of the AgH molecule (in cm^{-1}).

powers of $L(L+1)$ is required, with coefficients depending on the vibrational quantum number v. It should be noted, however, that such expansions are based on empirical rather than theoretical grounds. It will be shown below that assuming the moment of inertia depends on L will give results equivalent to those from the Dunham expansion. One can also try to relate the deviations of the real level energies from Eq. (21) to a deeper mathematical formalism, by introducing specific changes in the algebra defined by Eqs. (24), which is the basis of angular momentum theory.

The so-called *quantum* (or q-deformed) algebra $\mathrm{su}_q(2)$, which has been recently used with success to describe the backbending phenomenon in the AgH molecule [20], was introduced some time ago when trying to find exact solutions to some problems in statistical mechanics [27]. This ''quantum'' algebra is obtained by ''deforming'' su(2), introducing new angular momentum operators J_+, J_0, and J_- with *generalized* commutation relations

$$[J_0,J_\pm]=h_\pm(J_+,J_0,J_-), \quad [J_+,J_-]=k(J_+,J_0,J_-), \tag{27}$$

where $h_\pm$ and k are arbitrary functions. The uncertainty of these functions is raised by assuming the preservation of the similarity with the standard angular momentum theory. For instance, if J_0 is to describe the projection of the new angular momentum on the z axis, and J_+ and J_- are to play the role of raising and lowering operators for this momentum, one should accept that $h_\pm(J_+,J_0,J_-)$ coincides with $J_\pm$, meaning that the first of Eqs. (24) and (27) coincide. Analogous considerations lead to the conclusion that k must be a function of J_0 only, say $k_q(J_0)$, assuming this function depends on some parameter q in such a way that $k_q(J_0)\rightarrow J_0$ when $q\rightarrow 1$. This last requirement means that in the limit of $q\rightarrow 1$ the second of Eqs. (27) reduces to the second of Eqs. (24), ensuring the continuity of the new angular momentum with the old one. Here we should remember that correspondence principles play a strategic heuristic role when investigating new theories: for instance, relativistic mechanics goes into classical mechanics when the velocity of light c goes to infinity, and quantum mechanics goes into classical mechanics when the quantum of action h goes to zero. Similarly, a quantum algebra, supposedly appropriate for describing deformable systems, goes into the standard one, fit for describing rigid systems, when q goes to 1.

The function $k_q(J_0)$ can be further specified by imposing that the ''sum rule'' for the new angular momenta coincides with that for the old ones. This means that when adding two angular momenta given with quantum numbers J_1 and J_2 their sum should be given with a quantum number J satisfying the condition $|J_1-J_2|\leqslant J\leqslant|J_1+J_2|$. This requirement can be fulfilled by choosing for $k_q(J_0)$ a weighted difference of exponentials of $2J_0$ with q as the basis, q being necessarily a real number or a pure phase: $q=e^{\kappa}$ with κ real or imaginary. The resulting $\mathrm{su}_q(2)$ algebra, which can be considered as a q-deformation of the su(2) algebra for angular momentum operators, therefore involves three new generators, J_+, J_0, J_-, satisfying the generalized commutation relations [27]

$$[J_0,J_\pm]=\pm J_\pm,\quad [J_+,J_-]=\frac{e^{2\kappa J_0}-e^{-2\kappa J_0}}{e^{\kappa}-e^{-\kappa}}. \tag{28}$$

When the parameter κ is small, the second equation reduces to

$$[J_+,J_-]=2J_0+4\kappa J_0^2+O(\kappa^2), \tag{29}$$

which is quadratic in J_0 and yields the second of the linear equations (24) when $\kappa\rightarrow 0$. The quantum algebra $\mathrm{su}_q(2)$ can then be used for describing such deviations as inhomogeneities, anisotropies, and deformabilities of quantum systems from the standard symmetries described by the su(2) algebra.

If one introduces the q notation

$$[A]_q\equiv\frac{q^A-q^{-A}}{q-q^{-1}}\quad (q\equiv e^{\kappa}), \tag{30}$$

where A may be an operator as well as a number, the above commutation relations can be written in the form

$$[J_0,J_\pm]=\pm J_\pm,\quad [J_+,J_-]=[2J_0]_q, \tag{31}$$

which is formally analogous to Eq. (24). Because the argument κ of q in Eq. (30) may be either purely real (τ) or imaginary ($i\tau$), the q numbers (or operators) in these two cases take the respective forms

$$[A]_q=\begin{cases}\dfrac{\sinh(\tau A)}{\sinh(\tau)} & \text{if } q=e^{\tau}\quad \text{(a)}\\[2ex] \dfrac{\sin(\tau A)}{\sin(\tau)} & \text{if } q=e^{i\tau}\quad \text{(b)}\ .\end{cases} \tag{32}$$

In the limit $q\rightarrow 1$ (that is, $\tau\rightarrow 0$) one obtains

$$\lim_{q\rightarrow 1}[A]_q=A, \tag{33}$$

this entailing Eq. (31) to reduce to Eq. (24), and yielding, for the q generators ($m=+,0,-$),

$$\lim_{q\rightarrow 1}J_m=L_m\,. \tag{34}$$

While the square of the length of the angular momentum $\mathbf{L}^2$, i.e., the Casimir operator C_2 of the standard algebra su(2), is given by (25), the Casimir operator $C_2^q[\mathrm{su}_q(2)]$, which is defined similarly by the condition that all generators J_m should commute with it, has the form

$$C_2^q=J_-J_++[J_0]_q[J_0+1]_q, \tag{35}$$

which can also be interpreted as the square of the length $\mathbf{J}^2$ of a new, q-deformed, angular momentum operator J.

The similarity of the standard and quantum algebras entails a similarity in their representation theories. Jimbo [28] has shown that the IUR's $\mathcal{D}_q^J$ of $\mathrm{su}_q(2)$ are determined, by analogy with those $\mathcal{D}^J$ of su(2), by numbers $J=0,\ \frac{1}{2},\ 1,\ \frac{3}{2},\ldots$ and $M=-J,-J+1,\ldots,J$. These IUR's are derived from their highest-weight vector $|JJ\rangle_q$, which satisfies equations similar to the corresponding ones in su(2). The basis vectors of the representation space are obtained by successive applications of the lowering operator J_- on $|JJ\rangle_q$. Using the resulting normalization factor, one obtains

$$J_0|JM\rangle_q=M|JM\rangle_q\,,$$
$$J_\pm|JM\rangle_q=\sqrt{[J\mp M]_q[J\pm M+1]_q}|J,M\pm 1\rangle_q\,. \tag{36}$$

These expressions can be used to derive the eigenvalues of the q-deformed Casimir operator in terms of q numbers,

$$\langle C_2^q\rangle=[J]_q[J+1]_q\,. \tag{37}$$

As one can see, the properties of q-deformed states can be expressed in a way completely analogous to that for the standard states, the only difference being that the standard numbers occurring in the latter are replaced by q numbers in the former. However, one should be cautious in the applications because relations holding for ordinary numbers will not always hold for q numbers (e.g., $\frac{4}{2}=2$ but $[4]_e/[2]_e=7.52\ldots$).

2. Quantum description of rotational bands

Let us now consider how $\mathrm{su}_q(2)$ can be applied to a description of molecular rotational spectra. For a rigid symmetric top the Hamiltonian can be written in the form

$$H=\frac{1}{2\mathcal{J}_{xy}}\mathbf{L}^2+\left(\frac{1}{2\mathcal{J}_{zz}}-\frac{1}{2\mathcal{J}_{xy}}\right)L_z^2, \tag{38}$$

where $\mathbf{L}^2=L_x^2+L_y^2+L_z^2$ is the Casimir operator C_2 of su(2) and $\mathcal{J}_{zz}$ and $\mathcal{J}_{xy}$ are the axial and equatorial moments of inertia. The second term does not affect the arrangement of the levels within a band and can therefore be neglected, yielding the rigid top levels (21). Now it has been shown [29] that deformed nuclear rotational bands can be fitted very accurately using a Hamiltonian proportional to the Casimir operator C_2^q, which is derived from Eq. (38) by replacing the generators L_m by the q-deformed generators J_m, i.e.,

TABLE I. Nonsplit double q-rotator best-fit parameters for the lower rotational bands of the lower electronic state of AgH.

	$v''=0$	$v''=1$	$v''=2$	$v''=3$
A	6.3458	6.1463	5.9469	5.7476
τ_a	0.012 657	0.012 827	0.013 026	0.013 277
B	6.2654	6.1144	5.9438	5.7729
τ_b	0.012 106	0.012 680	0.013 052	0.013 540
C	1.2264	0.410 11	0.393 43	0.466 33
τ_c	1.3713	1.0369	0.642 51	0.597 10
E_0	51.413	28.136	6.8840	2.0193

TABLE II. Split single q-rotator best-fit parameters for the lower rotational bands of the lower electronic state of AgH.

	$v''=0$	$v''=1$	$v''=2$	$v''=3$
A^{even}	6.3461	6.1468	5.9487	5.7530
τ^{even}	0.012 662	0.012 837	0.013 059	0.013 366
A^{odd}	6.3454	6.1466	5.9481	5.7530
τ^{odd}	0.012 655	0.012 834	0.013 053	0.013 366

$$H^q = AC_2^q, \tag{39}$$

where A is a ''lightness'' constant related to a moment of inertia.

The eigenstates of the q-deformed rotator described by the Hamiltonian (39) are the above-defined $|JM\rangle_q$, and its energy levels are given by

$$E_q(J) = A[J]_q[J+1]_q$$
$$= \begin{cases} A\,\dfrac{\sinh(\tau J)\sinh[\tau(J+1)]}{\sinh^2(\tau)} & \text{if } q=e^{\tau} \quad (40a) \\[2ex] A\,\dfrac{\sin(\tau J)\sin[\tau(J+1)]}{\sin^2(\tau)} & \text{if } q=e^{i\tau}. \quad (40b) \end{cases}$$

These formulas differ from the standard formula (21) in the way that they describe the intervals between the states. If $|\tau|$ is not very large, the first formula gives an ''extended'' spectrum in which the level spacings become larger than in the standard bands, whereas the second formula gives a ''squeezed'' spectrum whose levels become closer. With increasing J the moment of inertia $\mathcal{J}$ of the (stretched) molecule (or nucleus) actually increases and the interval between the states becomes shorter, justifying the use of the second formula.

It is useful to make Taylor expansions of Eqs. (40) and sum up the coefficients of the terms containing the same powers of $J(J+1)$ (all other terms canceling out). For the second of these equations the final result is

$$E_q(J) = \frac{1}{2\mathcal{J}}\left\{ J(J+1) - \frac{\tau^2}{3}[J(J+1)]^2 + \frac{2\tau^4}{45}[J(J+1)]^3 - \frac{\tau^6}{315}[J(J+1)]^4 + \cdots \right\}, \tag{41}$$

where $1/2\mathcal{J} = (A\tau^2/\sin^2\tau)(1-\tau^2/3!+\ldots) \to A$ when $\tau \to 0$. This relation is of the form (22) used for fitting experimental spectra, except that now we have only two parameters, A and τ, instead of an unlimited number of expansion coefficients. Each term differs from the preceding one by a factor involving $-\tau^2$. For τ^2 to be of the observed order, 10^{-3}, $|\tau|$ should be around 0.03. It should be noted that, in order to guarantee that $E_q(J)$ be an increasing function of J, one must have, in Eq. (40b):

$$|\tau|(J+1) \leqslant \frac{\pi}{2}. \tag{42}$$

With $|\tau| = 0.0174$ as in HF, one finds $J \leqslant 89$ and with $|\tau| = 0.0113$ as in HBr, one finds $J \leqslant 138$ [24]. These limiting values are higher than the highest J values reported for diatomic molecules.

3. Physical interpretation of the deformation parameter

The ''variable moment of inertia'' (VMI) model, which is widely used in nuclear spectroscopy (Ref. [30] and references therein) and is also relevant to molecular spectroscopy, stems from the idea that the distances between particles in a many-particle system (and the resulting moment of inertia) increase with the value of the rotational quantum number, this generating an additional potential energy. The level energies in a rotational band are then given by

$$E(J) = \frac{J(J+1)}{2\mathcal{J}(J)} + \tfrac{1}{2}C(\mathcal{J}(J) - \mathcal{J}_0)^2, \tag{43}$$

with $\mathcal{J}(J)$ being the moment of inertia for angular momentum J, whereas C and $\mathcal{J}_0$ are potential-energy parameters to be fitted to the data: $\mathcal{J}_0$ is the ground-state moment of inertia, and it is meaningful to write C as a function of the ''softness'' parameter σ of the nucleus (or molecule):

$$C = \frac{1}{2\sigma\mathcal{J}_0^3}. \tag{44}$$

The moment of inertia at given J is determined through the variational condition

$$\left.\frac{\partial E(J)}{\partial \mathcal{J}(J)}\right|_{J\ \text{fixed}} = 0,$$

which is equivalent to the cubic equation

$$\mathcal{J}(J)^3 - \mathcal{J}(J)^2\mathcal{J}_0 - \frac{J(J+1)}{2C} = 0. \tag{45}$$

This equation has only one real root:

$$\mathcal{J}(J) = \frac{\mathcal{J}_0}{3} + \sqrt[3]{P+Q+R} + \sqrt[3]{P+Q-R},$$

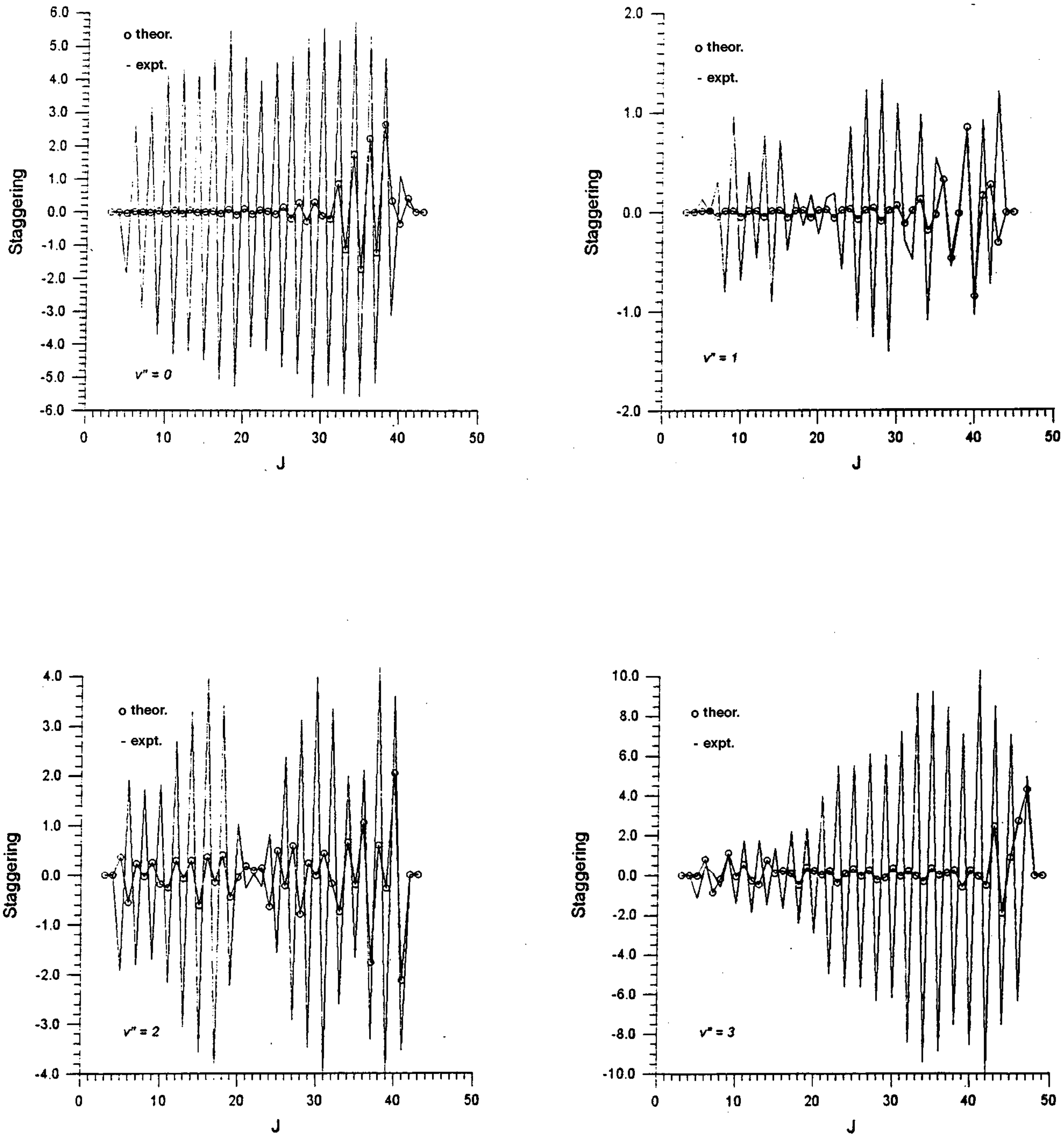

FIG. 6. Superposition of experimental (expt.) and theoretical (theor.) staggerings obtained using two regular, q-interacting, q rotators for the lower rotational bands $\nu''=0,12,3$ of the AgH molecule.

$$P=\frac{J(J+1)}{4C},\qquad Q=\frac{\mathcal{J}_0^3}{27},$$

$$R=\left(\frac{[J(J+1)]^2}{16C^2}+\frac{\mathcal{J}_0^3 J(J+1)}{54C}\right)^{1/2}.$$

Expanding the roots in the above expression, one obtains

$$\mathcal{J}(J)=\mathcal{J}_0\{1+\sigma J(J+1)-2\sigma^2[J(J+1)]^2+7\sigma^3[J(J+1)]^3 -30\sigma^4[J(J+1)]^4+\cdots\}. \tag{46}$$

Substituting Eq. (46) into Eq. (43) and expanding yields

$$E(J)=\frac{1}{2\mathcal{J}_0}\{J(J+1)-\tfrac{1}{2}\sigma[J(J+1)]^2+\sigma^2[J(J+1)]^3 -3\sigma^3[J(J+1)]^4+\cdots\}. \tag{47}$$

Comparing Eqs. (47) and (41) shows that the *ground-state moment of inertia* $\mathcal{J}_0$ of the VMI model is related to the inverse of the *lightness parameter* A of the quantum-group model, i.e., $\mathcal{J}_0\approx(1-\tau^2/3!+\cdots)/2A$, and that the *softness parameter* σ of the VMI model corresponds roughly to the square of the *deformation parameter* σ of the quantum-group model, i.e., $\tau^2\approx 3f(n)\sigma$ [where $f(n)$ is an increasing function of the rank n of the expansion]. Physically, this means

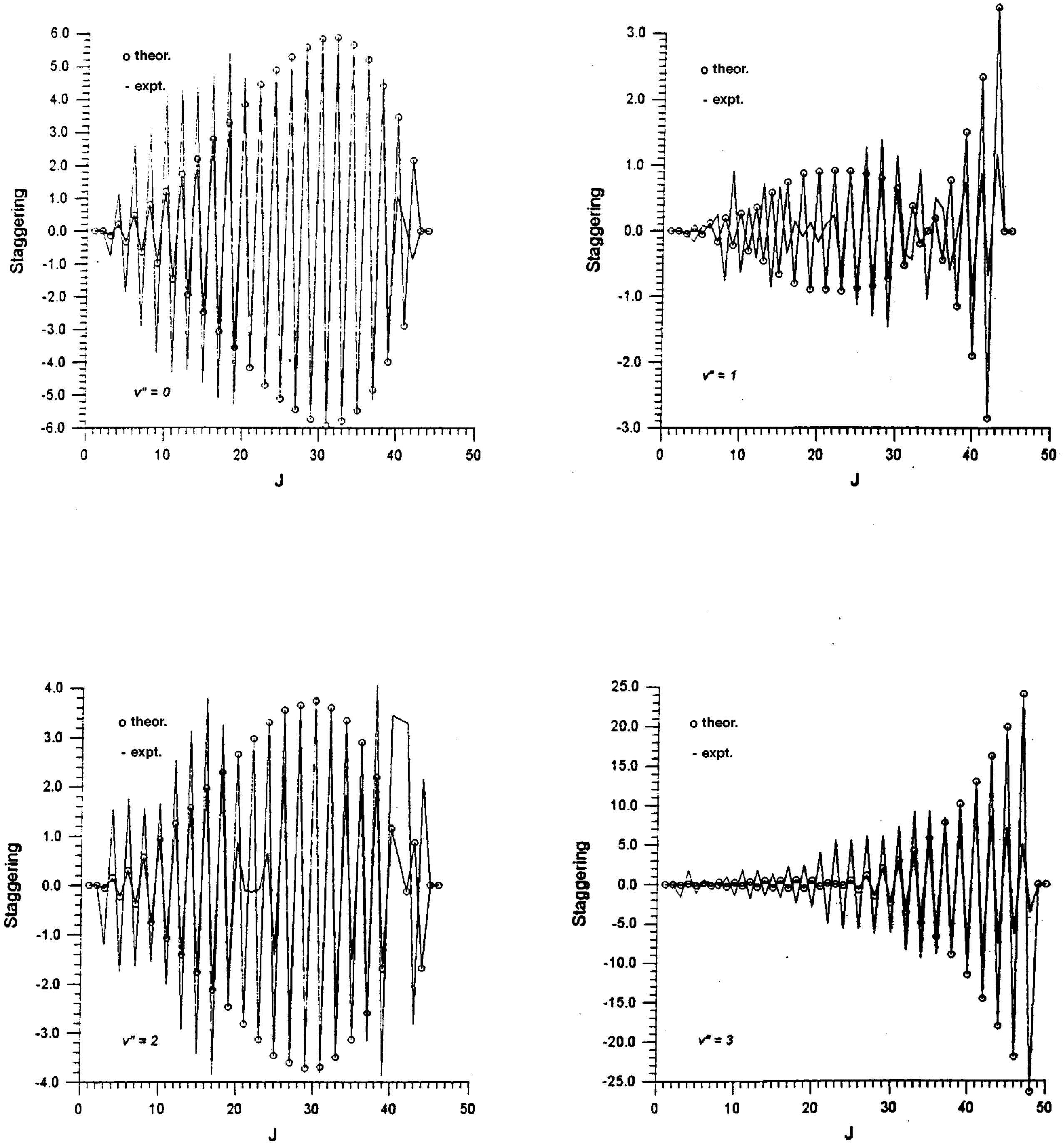

FIG. 7. Superposition of experimental (expt.) and theoretical (theor.) staggerings obtained using a single parity-split q rotator for the lower rotational bands $v''=0,1,2,3$ of the AgH molecule.

that quadrupling, for instance, the softness parameter σ in Eq. (47) has about the same effect as doubling the deformation parameter τ in Eq. (41). At this level, the quantum-group model can thus be viewed as an alternative formulation of the VMI model, the continuity introduced in the (otherwise discrete) commutation relations (28) expressing the progressivity of the variation of the moment of inertia with the rotational quantum number. Both models involve two parameters only but, contrary to the phenomenological VMI model, the quantum-group model has a deep mathematical structure, since it involves a natural (though untrivial) generalization of the group algebra used in angular momentum theory.

C. Backbending and staggering in terms of two interacting rotators

We have already stated that Eq. (40) with $q=e^{i\tau}$ for the quantum rotator gives a very good description of rotational spectra of diatomic molecules. In particular, this formula (replacing A by $1/J$) describes fairly well the ''upbending'' phenomenon [20]. However, it cannot explain ''backbending,'' for which the interaction between two rotational bands must be considered [20].

It can be checked easily that Eq. (40b) cannot explain staggering either. If one inserts Eq. (40b) into the staggering formula (9), one obtains the expression of a smooth curve (of sine type), which does not change its sign over the variation interval of the angular momentum and whose amplitude is 2–3 orders of magnitude smaller than that of the observed staggering. Writing

$$\widetilde{E}(J)=\overline{E(J)}+\delta E(J), \tag{48}$$

where $\widetilde{E}(J)$ is the observed value of the energy level, $\overline{E(J)}$ the smooth variation given by Eq. (40b), and $\delta E(J)$ the oscillating deviation from Eq. (40b), then, inserting Eq. (48) into Eq. (9), one finds the contribution of $\overline{E(J)}$ to staggering vanishes, meaning that staggering can only originate from $\delta E(J)$. In order to describe staggering, one must then be able to calculate the deviations of energy levels from those predicted with the formula for the single q-deformed rotator. We shall investigate how far this can be done using models involving two interacting rotators.

According to the single-rotator model recalled in Sec. IV B 2, in each of its vibronic states the molecule can be considered as a rotator with a variable moment of inertia, i.e., a quantum (q-deformed) rotator with moment of inertia $\mathcal{J}_a$ and deformation parameter τ_a. The transitions between the levels within these different quantum rotators yield the observed rovibronic spectrum. The occurrence of ''backbending'' and the deviations $\delta E(J)$ in Eq. (50) both show that this model is not sufficient. We have already seen [20] that in order to explain ''backbending'' each of the q-deformed rotators (each rotational band) can be assumed to ''interact'' with another rotator with higher energy, which can be seen as a resultant of residual rotational motions. This higher-energy rotator is not directly observable (via transitions in the rovibronic spectrum), and in this sense plays an auxiliary role in the explanation of the rotational bands. It can also be characterized by a moment of inertia $\mathcal{J}_b$ and deformation parameter τ_b.

In the ''standard'' (non q-deformed) quantum mechanics this double-rotator model can be described in the following way. Let us denote by $\mathcal{J}_a$ and $\mathcal{J}_b$ the moments of inertia and by $\mathbf{L}_a$ and $\mathbf{L}_b$ the angular momenta of the two rotators. Their Hamiltonians take the forms

$$\hat{H}_a=\frac{1}{2\mathcal{J}_a}\,\mathbf{L}_a^2,\quad \hat{H}_b=\frac{1}{2\mathcal{J}_b}\,\mathbf{L}_b^2+E_0, \tag{49}$$

where the constant E_0 defines the zero energy for the second rotator. The energies of the two rotators, when their interaction is neglected, are given by

$$E_a(J)=\frac{1}{2\mathcal{J}_a}\,J(J+1),\quad E_b(J)=\frac{1}{2\mathcal{J}_b}\,J(J+1)+E_0. \tag{50}$$

If the interaction $\hat{H}_{ab}$ is now taken into account, the levels E_a and E_b yield two new split levels:

$$E_\pm(J)=\frac{E_a+E_b}{2}\pm\left[\left(\frac{E_a-E_b}{2}\right)^2+\left|\langle\hat{H}_{ab}\rangle\right|^2\right]^{1/2}. \tag{51}$$

Here the minus sign corresponds to the resulting lower energy: as the observable transitions take place between the lower levels of the rotators, it is important to know only how these levels change under the interaction; only the minus sign, which defines the so-called yrast line, will thus be considered hereafter.

An explicit form of $\langle\hat{H}_{ab}\rangle$ could be obtained from microscopic calculations. However, in this phenomenological model of two interacting rotators, a simple form of $\langle\hat{H}_{ab}\rangle$ can be derived from symmetry considerations. The interaction term (as the system Hamiltonian as a whole) must be invariant under all space rotations. Now we have at our disposal only two vector operators $\hat{\mathbf{L}}_a$ and $\hat{\mathbf{L}}_b$ with which to build the interaction operator $\hat{H}_{ab}$. The only scalar expression which can be built from these vectors is their scalar product

$$\hat{H}_{ab}=2k\hat{\mathbf{L}}_a\cdot\hat{\mathbf{L}}_b=k(\hat{\mathbf{L}}^2-\hat{\mathbf{L}}_a^2-\hat{\mathbf{L}}_b^2), \tag{52}$$

where $\hat{\mathbf{L}}=\hat{\mathbf{L}}_a+\hat{\mathbf{L}}_b$, and k is a constant which can be calculated or measured. If we take into account the fact that the two involved rotators have the same angular quantum number, $J_a=J_b$, and that they are coupled to give an angular quantum number $J=J_a=J_b$ for which the energy of the system is minimal, we obtain

$$\langle\hat{H}_{ab}\rangle=-kJ(J+1), \tag{53}$$

which is in agreement with an assumption previously made to describe backbending in nuclei [30] and molecules [20].

Similar considerations can be held for two ''quantum'' (q-deformed) rotators. The energies of the two rotators are now given by

$$E_{q_a}(J)=A[J]_{q_a}[J+1]_{q_a},\quad [x]_{q_a}=\frac{\sin\tau_a x}{\sin\tau_a}, \tag{54}$$

$$E_{q_b}(J)=B[J]_{q_b}[J+1]_{q_b}+E_0,\quad [x]_{q_b}=\frac{\sin\tau_b x}{\sin\tau_b}. \tag{55}$$

Here also a phenomenological form for the (q-deformed) interaction operator $\hat{H}^q_{ab}$ can be derived from the symmetry condition that it should be rotational invariant and must be built from the (q-deformed) angular momentum operators $\mathbf{L}^q_a$ and $\mathbf{L}^q_b$. Due to the specific rules for the addition of q-deformed angular momenta (see, e.g., Ref. [26]), the only scalar operator that can be used for building $\hat{H}^q_{ab}$ is the Casimir operator $C^q_2[\mathrm{su}_q(2)]$, formed from the sum of the angular momenta of the two quantum rotators. Taking into account the fact that in this case one also has $J=J_1=J_2$, one obtains

$$\langle H^{q_c}_{ab}\rangle=C[J]_{q_c}[J+1]_{q_c},\quad [x]_{q_c}=\frac{\sin\tau_c x}{\sin\tau_c}, \tag{56}$$

where τ_c is a (q-deformed) interaction parameter (different from τ_a and τ_b). The values of both C and τ_c can be determined by fitting experimental data.

V. SIMULATIONS AND RESULTS

We have seen in Sec. IV C that, unlike ''upbending,'' staggering as defined in Eq. (9) cannot be described using the single q-rotator levels given in Eq. (40b), which yield only

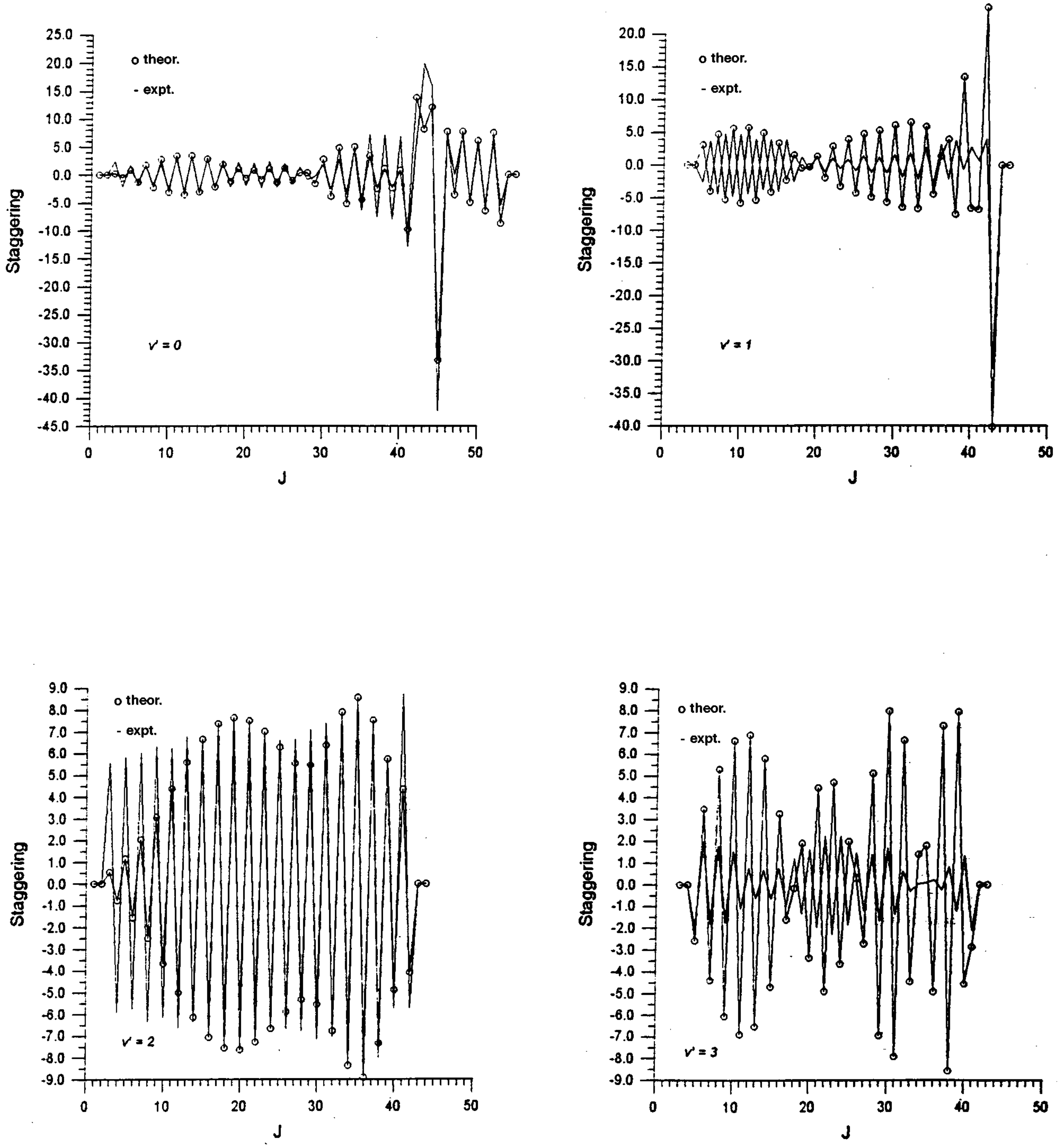

FIG. 8. Superposition of experimental (expt.) and theoretical (theor.) staggerings obtained using two parity-split, q-interacting, q rotators for the upper rotational bands $v'=0,1,2,3$ of the AgH molecule.

smooth periodic variations of $\Delta E_t(J)$—rather similar to the wide envelopes noted in Figs. 3–5. We now show through computer simulations that, unlike ‘‘backbending,’’ staggering cannot either be properly described using the standard double q-rotator model. We have used the energy levels of the yrast line $E_-(J)$ from Eq. (51) with E_a, E_b, and $\langle \hat{H}_{ab} \rangle$ replaced by E_{q_a}, E_{q_b}, and $\langle \hat{H}_{ab}^{q_c} \rangle$ from Eqs. (54), (55), and (56), respectively. We have performed fittings of the involved energy levels of the lower rotational bands of the lower electronic state in order to find to which extent the second q rotator could be effective in explaining staggering, which occurs even before ‘‘upbending’’ takes place.

The best-fit values of the seven parameters involved in this model for $v''=0$, 1, 2, 3 are given in Table I, and the staggering curves calculated from them are compared to those derived from the measured transitions in Fig. 6. The parameters of the two rotors are closer, and those of the interaction smaller, than in the case of the upper levels [20], where strong perturbations are present. The theoretical staggering amplitudes appear much smaller than the experimental ones, especially for the low values of J, and are alternatively in phase and out of phase with them, changes occurring around the nodes of the staggering envelopes discussed in Sec. III. Thus it appears that neither molecular (or

TABLE III. Split double q-rotator best-fit parameters for the lower rotational bands of the upper electronic state of AgH.

	$\nu'=0$	$\nu'=1$	$\nu'=2$	$\nu'=3$
A^{even}	6.1177	5.7616	5.3408	4.8443
τ_a^{even}	0.014 604	0.015 135	0.016 881	0.015 804
B^{even}	2.9498	39.480	21.917	17.457
τ_b^{even}	0.012 946	0.075 232	0.090 785	0.094 590
C^{even}	2.2494	0.920 61	0.910 82	2.5383
τ_c^{even}	6.1727	0.027 419	0.026 278	0.029 186
E_0^{even}	5141.3	10 048.0	8028.5	14814.0
A^{odd}	6.1189	5.7720	5.3435	4.8371
τ_a^{odd}	0.0146 32	0.014 740	0.016 983	0.021 023
B^{odd}	2.9191	43.793	22.121	8.5960
τ_b^{odd}	0.0127 81	0.073 918	0.090 717	0.097 498
C^{odd}	2.2206	1.4679	0.897 50	3.4321
τ_c^{odd}	6.1736	0.036 761	0.0261 35	0.025 216
E_0^{odd}	5186.0	10 025.	8026.2	14 869.0

nuclear) nonrigidity, nor level noncrossing—very well accounted for with the single and double q-rotator models, respectively [20]—are sufficient to explain the systematic parity splitting revealed by the staggering effect.

Therefore we have allowed for parity splitting in our formalism, i.e., we have fitted the energies independently for the odd and even states (for the lower and upper bands as well) and obtained parity-split values for the parameters A and τ. With this extension it is expected that some staggering can be obtained even within the standard model, but the quantum model remains in order to reproduce the ''upbending'' and ''backbending'' curves (Fig. 2, right column). As a single q rotator proved sufficient for the lower levels, which display only ''upbending'' [20], we have used only one split (odd-even) q rotator for $\nu''=0$, 1, 2, 3 (involving four parameters), while, as a double q rotator was necessary for the upper levels, which display also ''backbending'' [20], we used a pair of split q rotators for $\nu'=0$, 1, 2, 3 (14 parameters).

For the lower bands we first fitted the even state energies ($J=2,4,6,\ldots$), obtained as explained in Sec. II, by Eq. (40b), then used the A and τ parameters thus obtained to derive an estimate of $E(1)$:

$$E_{q^{\mathrm{ev}}}(1)=A^{\mathrm{ev}}\,\frac{\sin 2\tau^{\mathrm{ev}}}{\sin\tau^{\mathrm{ev}}}=2A^{\mathrm{ev}}\cos\tau^{\mathrm{ev}}, \tag{57}$$

then used this value of $E(1)$ to derive, from the experimental transition energies, the odd level energies ($J=3,5,\ldots$). These latter were subsequently fitted to Eq. (40b), yielding the odd A and τ parameter values. The differences between the even and odd A and τ values, displayed in Table II, are less than 10^{-3} and 10^{-5}, respectively. The staggering curves calculated from the energies of the even and odd states thus fitted independently are compared to those derived from the measured transition energies in Fig. 7. The theoretical staggering amplitudes appear much closer to and more in phase with the experimental ones than in the previous model, but the periodic patterns of the envelopes noted in Sec. III are not very satisfactory.

For the upper bands we applied the same procedure as above, fitting first the even-and then the odd-state energies, but using now two q-interacting q rotators. As in the nonsplit model first used for the lower bands, we used the energy levels of the yrast line $E_-(J)$ from Eq. (51) with E_a, E_b and $\langle\hat{H}_{ab}\rangle$ replaced by E_{q_a}, E_{q_b} and $\langle\hat{H}_{ab}^{q_c}\rangle$ from Eqs. (54), (55) and (56), respectively. The formula used to derive $E(1)$ is then

$$\begin{aligned}E_-^{\mathrm{ev}}(1)={}&(A^{\mathrm{ev}}\cos\tau_a^{\mathrm{ev}}+B^{\mathrm{ev}}\cos\tau_b^{\mathrm{ev}})-[(A^{\mathrm{ev}}\cos\tau_a^{\mathrm{ev}}\\&-B^{\mathrm{ev}}\cos\tau_b^{\mathrm{ev}})^2+(C^{\mathrm{ev}}\cos\tau_c^{\mathrm{ev}})^2]^{1/2}.\end{aligned} \tag{58}$$

The differences between the even and odd A, B, C, and E_0 and τ_a, τ_b, and τ_c values, displayed in Table III, are much larger than for the lower bands (about 0.02% to 100% for the A's and about 0.2% to 30% for the τ's). The average even-odd values from this table are close to but more accurate than the nonsplit values given in Table 2 of our previous work [20], because here we use a ''quantum'' interaction instead of the ''standard'' interaction used the previous work. The staggering curves calculated from the even- and odd-state energies thus fitted independently are compared to those derived from the measured transition energies in Fig. 8. In spite of some remaining differences in the amplitudes and phases, especially in the vibrationally odd bands ($\nu'=1,3$), the ''theoretical'' staggering curves seem quite similar to the ''experimental'' ones, now including the periodic patterns of the envelopes.

The fact that involving a second, q-interacting, q rotator improves considerably, though not decisively, the fits of the upper bands, compared to those of the lower bands, might mean the second rotator, even though not significant in describing a ''gross'' phenomenon like ''upbending'' for the lower bands, might play a critical role in describing the ''fine'' structure of staggering. But it should also be remembered that any reasonable function involving 14 parameters will give better fits of a set of experimental data than a similar function with only four parameters. In addition, the remaining discrepancies, particularly for odd values of ν, hint

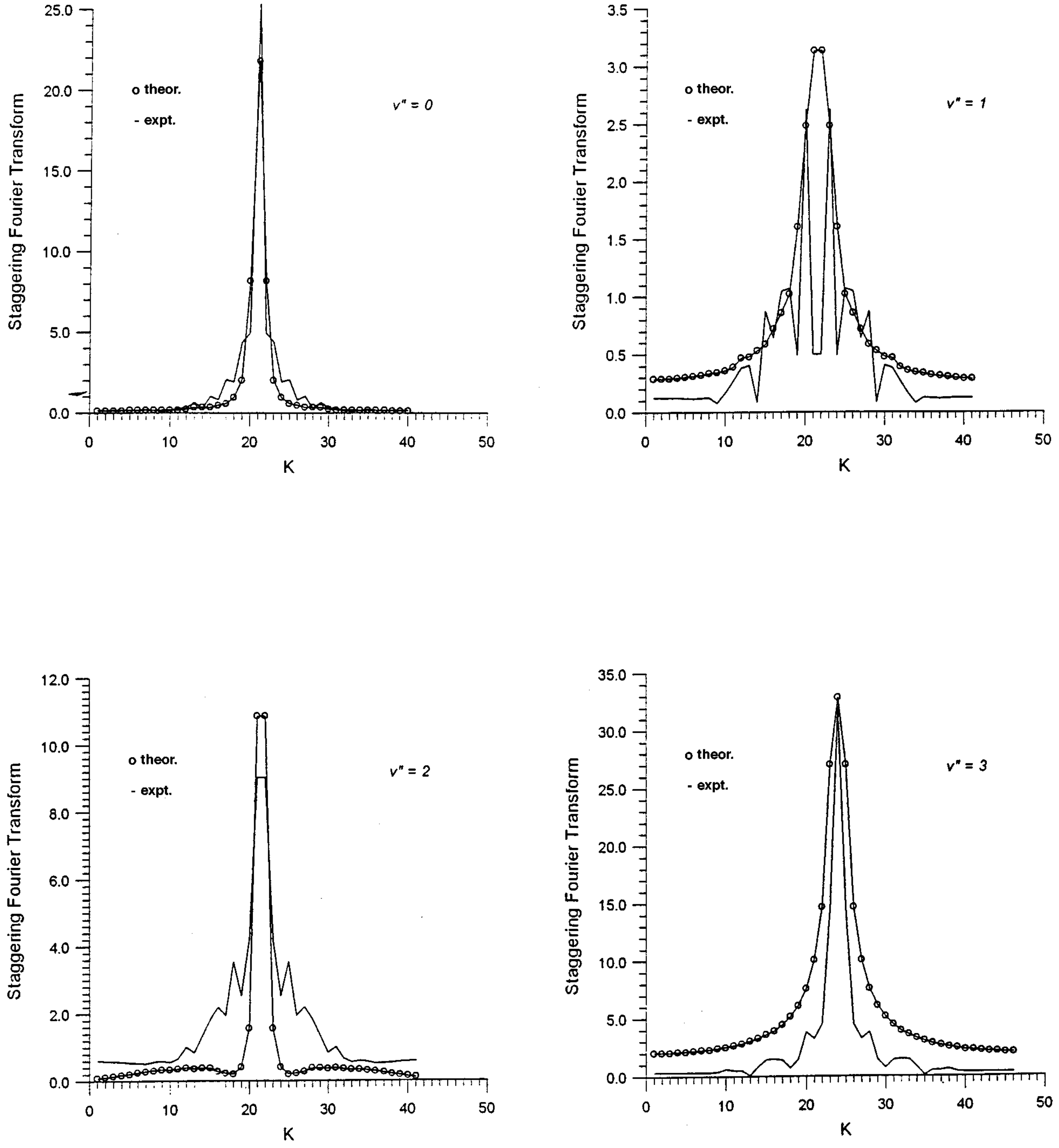

FIG. 9. Superposition of the Fourier transforms of experimental (expt.) and theoretical (theor.) staggerings from the single parity-split q rotator for the bands $\nu''=0,1,2,3$ of the AgH molecule (K is the dimensionless conjugate of J).

it might be necessary to improve the model by involving q rovibrators [31] or even qp rovibrators [32], but such extensions would increase further the number of parameters, and accordingly reduce the significance of the fits.

A Fourier analysis was performed on both the ''experimental'' and ''theoretical'' staggering curves shown in Figs. 7 and 8. The corresponding Fourier transform curves are displayed in Figs. 9 and 10, respectively. Remembering that sine and δ functions are Fourier transforms of each other, the main peaks (usually one or two) in the Fourier transform curves can be related to the main harmonics in the corresponding staggering curves, and the side wiggles to secondary harmonics. Even for the lower bands our model seems to reproduce fairly well the envelopes of the Fourier curves, and for the upper bands it also reproduces some of the side wiggles. The best results are obtained for $\nu'=0$, 2 and $\nu''=0$, 3, and the worse for $\nu'=3$ and $\nu''=1$, this reinforcing the idea that a model involving q rovibrators might allow better fittings.

VI. DISCUSSION AND CONCLUSION

In this paper we have shown that not only the long-known backbending phenomenon, but also the recently discovered staggering effect can, similarly as in nuclei, be observed in molecules. $\Delta J=2$ staggering has been shown for several ro-

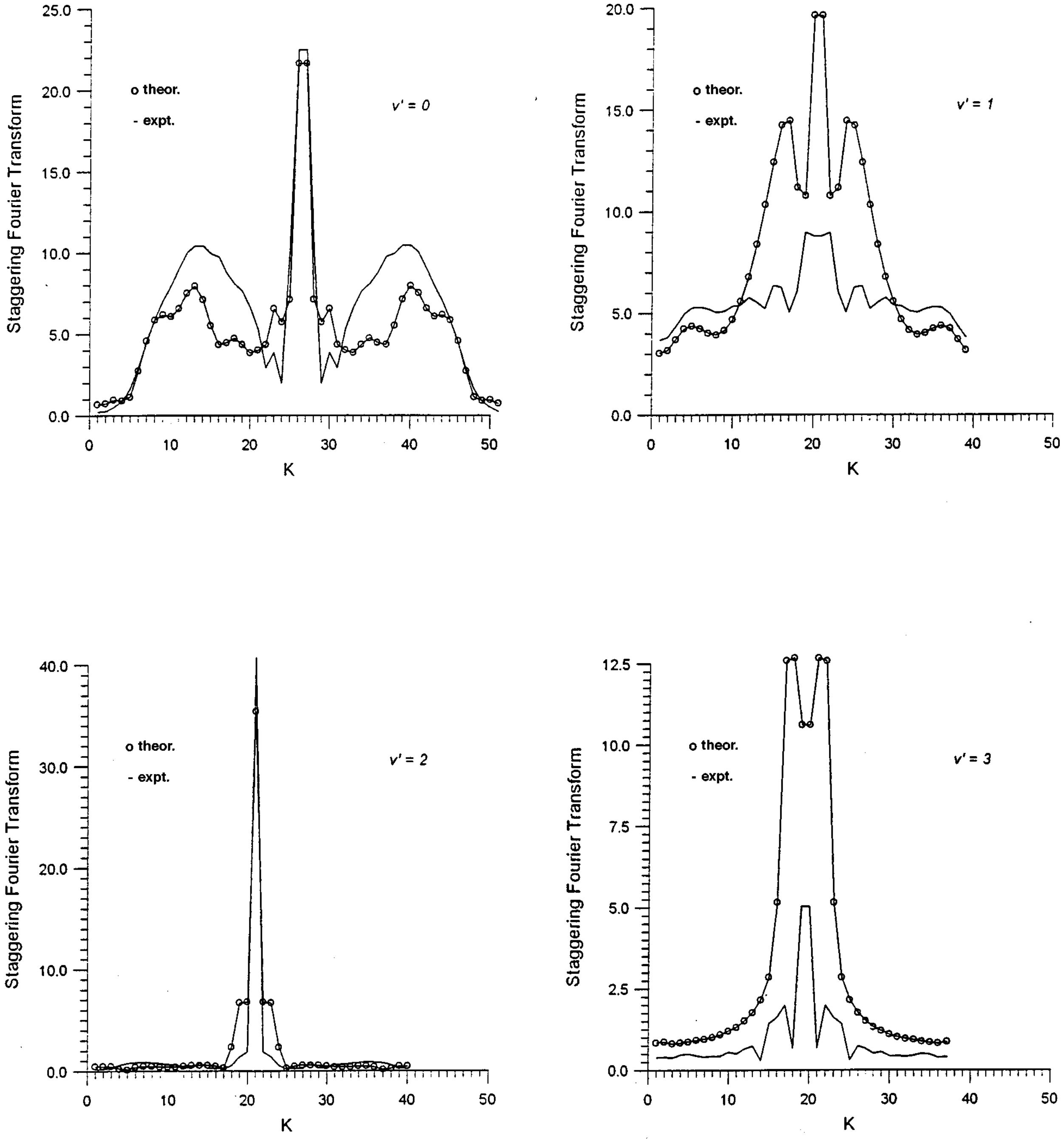

FIG. 10. Superposition of the Fourier transforms of experimental (expt.) and theoretical (theor.) staggerings from the two parity-split, q-interacting, q rotators for the bands $\nu' = 0,1,2,3$ of the AgH molecule (K is the dimensionless conjugate of J).

tational bands of the AgH molecule, where it already appears at quite low values of J and shows a rather complex structure involving amplitude modulation through various harmonics. The fitting of the experimental data reveals a small but significant parity dependence of the parameters A and τ, which define the q rotators used to describe the rotational levels, for both the lower and upper electronic states. From our tentative simulations using q-deformed rotators, which proved less efficient than for describing backbending [20], it appeared that (i) it is necessary to allow for parity splitting in the formalism to obtain any significant staggering; (ii) at least two q-interacting, q-deformed rotators are necessary, not only for the upper levels, where strong perturbations show up in the form of backbending, but also for the lower levels, where perturbations are too weak to yield backbending but may be critical in describing staggering; and (iii) the involvement of q vibrations coupled with q rotations, possibly in the form of qp rovibrators, might show more efficiency in yielding a satisfactory description of the staggering phenomenon.

There remains to find a physical explanation for this effect, particularly for the parity splitting which appears to be its main source. It would be surprising that this latter meant that a molecule may have an effective moment of inertia varying upon J in a parity-dependent manner. Intricate crossing of molecular levels or dynamical breaking of molecular symmetries, as in those quantum bifurcations at diabolic points investigated for spherical-top molecules [15,16], could be considered for a microscopic explanation of this effect. However, the detailed investigation of such possibilities requires more complete and more accurate experimental data. Now, while numerous papers provide thorough determinations of rotational constants (e.g., Ref. [33]), good raw experimental data are scarcer (e.g. Ref. [34]).

Other, preliminary results have been obtained recently [35] from an analysis of limited sets of spectroscopic data on a sample of diatomic molecules. The fact that staggering was evidenced in such diatomics as CoH or YD (but not CS) [35(a)] as well as in I_2 [35(b)]—irrespective of open-shell structure or top asymmetry—points to a rather general mechanism. From the magnitude of the deviations from pure rotational levels and the irregularity of the deviation amplitudes as a function of J in both CoH and YD, where the data—as in AgH—come from transitions involving electronic excitations, and from the absence of a significant effect—larger than experimental errors—in CS, where the data involve no electronic excitations, it has been suggested [35(a)] that staggering may have its source in interactions with nearby bands and/or crossings between interacting bands. If this is true, staggering simply reveals—in a spectacular way indeed—interband interactions and/or band crossings rather than some new symmetry breaking, as it was suggested for nuclei [10–14]. However, the present paper has shown that the model of two q-interacting, q rotators, which accounts very well for both upbending and backbending, is not sufficient to reproduce the observed staggering, which shows up even at low values of J. It remains to be proven that multiple q-interacting q rotators may yield similar results as the parity-split, double q-rotator model.

Our next steps will be to lead a thorough investigation of the properties of staggering in the standard rotational bands of I_2 and Te_2 [34], to check if an improved qp rovibrator [32] could prove more efficient in the description of this effect, and to attempt a semiquantitative explanation of the observed results through models involving both multiple-level crossing and symmetry breaking.

ACKNOWLEDGMENTS

Peter Raychev was supported by the Bulgarian Ministry of Science and Education under contracts Φ-417 and Φ-547, and by the French Ministry of Science and Technology through a senior-scientist fellowship. Jean Maruani was supported by the CNRS-BAS and UPMC-SKOU franco-bulgarian exchange conventions.

[1] G. Herzberg, *Spectra of Diatomic Molecules*, Molecular Spectra and Molecular Structure Vol. 1 (Van Nostrand, Toronto, 1950).

[2] I. Kovàcs, *Rotational Structure in the Spectra of Diatomic Molecules* (Hilger, London, 1969).

[3] H. Lefebvre-Brion and R. W. Field, *Perturbations in the Spectra of Diatomic Molecules* (Academic, Orlando, FL, 1986).

[4] A. Bohr and B. R. Mottelson, *Nuclear Structure* (Benjamin, Reading, MA, 1975), Vol. 2.

[5] P. Ring and P. Schuck, *The Nuclear Many-Body Problem* (Springer, Berlin, 1980), Vol. 1.

[6] P. J. Twin, B. M. Nyakò, A. H. Nelson *et al.*, Phys. Rev. Lett. **57**, 811 (1986); P. J. Nolan and P. J. Twin, Annu. Rev. Nucl. Part. Sci. **38**, 533 (1988); R. V. F. Janssens and T. L. Khoo, *ibid.* Annu. Rev. Nucl. Part. Sci. **41**, 5186 (1991); **211**, 5186 (1991); M. Meyer and J. P. Vivien, Ann. Phys. (N.Y.) **17**, 11 (1992).

[7] S. Flibotte, H. R. Andrews, G. C. Ball *et al.*, Phys. Rev. Lett. **71**, 4299 (1993); S. Flibotte, G. Hackman, I. Ragnarsson *et al.*, Nucl. Phys. A **584**, 373 (1995).

[8] B. Cederwall, R. V. F. Janssens, M. J. Brinkman *et al.*, Phys. Rev. Lett. **72**, 3150 (1994).

[9] Yang Sun, Jingye Zhang, and Mike Guidry, Phys. Rev. Lett. **75**, 3398 (1995).

[10] I. Hamamoto and B. Mottelson, Phys. Lett. B **333**, 294 (1994).

[11] A. O. Macchiavelli, B. Cederwall, R. M. Clark *et al.*, Phys. Rev. C **51**, R1 (1995).

[12] I. M. Pavlichenkov and S. Flibotte, Phys. Rev. C **51**, R640 (1995).

[13] I. N. Mikhailov and P. Quentin, Phys. Rev. Lett. **74**, 3336 (1995).

[14] F. Donau, S. Frauendorf, and J. Meng, Phys. Lett. B **387**, 667 (1996).

[15] W. G. Harter, C. W. Patterson, and J. J. da Paixao, Rev. Mod. Phys. **50**, 37 (1978); W. G. Harter and C. W. Patterson, J. Chem. Phys. **80**, 4241 (1984); W. G. Harter, Comput. Phys. Rep. **8**, 321 (1988).

[16] I. M. Pavlichenkov and B. I. Zhilinskii, Chem. Phys. **100**, 339 (1985); Ann. Phys. (N.Y.) **184**, 1 (1988); V. B. Pavlov-Verevkin, D. A. Sadovskii, and B. I. Zhilinskii, Europhys. Lett. **6**, 573 (1988); D. A. Sadovskii, and B. I. Zhilinskii, Mol. Phys. **65**, 109 (1988); G. Pierre, D. A. Sadovskii, and B. I. Zhilinskii, Europhys. Lett. **10**, 409 (1989).

[17] D. Bonatsos, C. Daskaloyannis, S. B. Drenska, G. A. Lalazissis, N. Minkov, P. P. Raychev, and R. P. Roussev, Phys. Rev. A **54**, R2533 (1996).

[18] L. Gerö and R. Schmid, Z. Phys. **121**, 459 (1943).

[19] U. Ringström and N. Åslund, Ark. Fys. **32**, 19 (1965).

[20] L. P. Marinova, P. P. Raychev, and J. Maruani, Mol. Phys. **82**, 1115 (1994).

[21] L. J. Dunham, Phys. Rev. **41**, 721 (1932).

[22] P. M. Morse, Phys. Rev. **34**, 57 (1929).

[23] L. Lathouvers and P. van Leuven, Chem. Phys. Lett. **70**, 410 (1980).

[24] D. Bonatsos, P. P. Raychev, R. P. Roussev, and Yu. F. Smirnov, Chem. Phys. Lett. **175**, 300 (1990).

[25] M. Kibler and T. Negadi (unpublished).

[26] P. Raychev, Adv. Quantum Chem. **26**, 239 (1995).

[27] P. P. Kulish and N. Reshetikhin, J. Sov Mat. Dokl. **23**, 2435 (1983).

[28] M. Jimbo, Lett. Math. Phys. **11**, 247 (1986).

[29] P. P. Raychev, R. P. Roussev, and Yu. F. Smirnov, J. Phys. G **16**, L137 (1990).

[30] D. Bonatsos, Phys. Rev. C **31**, 2256 (1985).

[31] D. Bonatsos, E. N. Argyres, and P. P. Raychev, J. Phys. A **24**,

L403 (1991); Z. Chang and H. Yan, Phys. Lett. A **158**, 242 (1991).

[32] M. R. Kibler, in *Symmetry and Structural Properties of Condensed Matter*, edited by W. Florck (World Scientific, Singapore, 1993); R. Barbier and M. Kibler, in *Modern Group Theoretical Methods in Physics*, edited by J. Bertrand (Kluwer, Dordrecht, 1995).

[33] M. M. Hessel and C. R. Vidal, J. Chem. Phys. **70**, 4439 (1979); R. A. Bernheim, L. P. Gold, C. A. Tomczyk, and C. R. Vidal, *ibid.* **87**, 861 (1987).

[34] S. Gerstenkorn and P. Luc, *Atlas du Spectre d'Absorption de la Molécule d'Iode* (CNRS, Paris, 1980); J. Cariou and P. Luc, *Atlas du Spectre d'Absorption de la Molécule de Tellure* (CNRS, Paris, 1980).

[35] (a) D. Bonatsos, C. Daskaloyannis, S. B. Drenska, J. Maruani, P. P. Raychev, and R. P. Roussev (to be published); (b) J. Maruani, S. B. Drenska, P. P. Raychev, and D. Bonatsos (unpublished).