

A Parameter to Quantify Molecular Quasilinearity^{1,2}

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A simple parameter is proposed for expressing the quasilinearity of molecules in a quantitative way. The parameter γ_0 is defined on the basis of a discussion of the separation of variables in the Born-Oppenheimer approximation. The parameter γ_0 assumes the value +1 for bent molecules and -1 for linear molecules. The range from -1 to +1 traces the transition of a vibrational degree of freedom in the linear configuration of a polyatomic molecule into a rotational degree of freedom in the bent configuration. The sequence of molecules along this parameter is shown and model calculations are carried out to further illustrate the physical interpretation of the parameter.

I. Introduction

Since the quasilinear formalism was first discussed by Thorson and Nakagawa¹ and Dixon², several molecules have been found to show quasilinearity. Johns³ discussed the effect of quasilinearity in some triatomic molecules and the linear-bent correlation of the rovibrational energy levels. By extending the linear-bent energy level correlation diagram to four-atomic molecules, Yamada, Nakagawa and Kuchitsu⁴ and Yamada, Winnewisser and Winnewisser⁵ could predict the symmetry properties and describe the allowed interactions in quasilinear four-atomic molecules successfully.

It might be useful, for extending the concept of the linear-bent correlation, to order the molecules in a sequence using a parameter which quantifies the quasilinearity, and which runs from the bent limiting molecular model to the linear limiting molecular model. For such a purpose it is desired to have a numerical parameter indicating the quasilinearity analogous to Ray's asymmetry parameter⁶ which indicates the inertial asymmetry of a molecule.

Quasilinearity depends on the potential function of the bending vibration concerned, and the quasilinearity parameter which we need should be a function of the potential parameters. It is, however, difficult to describe the potential function for those molecules which are of interest at an early stage of their study.

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A simple parameter which quantifies quasilinearity is proposed here on the basis of a discussion of the separation of variables in the Born-Oppenheimer approximation. To simplify the problem we discuss only triatomic molecules. The discussion can be extended for poly-atomic molecules directly by carefully assigning the bending mode which is concerned in this discussion, and assuming all other bending coordinates fixed.

II. Quantification of Molecular Quasilinearity

In a triatomic linear molecule one of the three rotational degrees of freedom can not be separated from the bending vibration. On the other hand in a bent molecule, all three rotational degrees of freedom can be well separated from the bending vibration. A quasilinear molecule should lie between these two limiting cases of the molecular models. Therefore, if we can define a numerical parameter which represents the validity of the separation of the variables of the bending vibration and of the coupled rotation, this parameter might be used for ordering molecules from the bent limit through the quasilinear model to the linear limit.

From the discussion of the Born-Oppenheimer approximation⁷ the order of magnitude for vibrational energy differences ΔE_v and that for rotational energy differences ΔE_r should be

$$\Delta E_r \sim \kappa^2 \Delta E_v \quad (1)$$

for the validity of the separation of the variables, where κ is equal to the ratio (electron-mass/proton-mass)^{1/4} which is called the Born-Oppenheimer constant.

Now we define the parameter γ as the ratio of these two energy differences:

$$\gamma = \Delta E_r / \Delta E_v. \quad (2)$$



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Then from the validity condition, Eq. (1), we obtain

$$\gamma \sim \kappa^2 \sim 10^{-2} \quad (3)$$

for a molecule for which the separation of the two variables concerned is valid. For the limiting case of a bent molecule we choose to use the fundamental frequency ν_{bend} of the bending vibration and the rotational constant A for ΔE_v and ΔE_r , respectively:

$$\gamma = A/\nu_{\text{bend}}. \quad (4)$$

Strictly speaking the rotational constant A approximates the rotational energy difference in the prolate top limit between $K_a = 0$ and 1, $A - \frac{1}{2}(B + C)$. For the quasilinear molecule in which we are really interested, the rotation about the a -axis, the axis of smallest moment of inertia, is coupled with the bending vibration and the rotational constant A represents well the rotational energy difference required in Equation (2). Thus for simplicity the rotational constant A is used here for all molecules to represent ΔE_r .

From a linear-bent energy level correlation diagram given in Fig. 1 it is seen that the ratio defined above corresponds to the ratio

$$\gamma = E(0, 1^1, 0)/E(0, 2^0, 0) \quad (5)$$

using the quantum numbers of a linear molecule. $E(v_1, v_2^l, v_3)$ is the vibrational energy level mea-

sured from the ground vibrational state, $E(0, 0^0, 0)$. An extensive discussion of the energy level correlation diagram is given in References 4, 5, 8. Equations (4) and (5) can both be expressed by

$$\gamma = \frac{E(\text{lowest state with } K, \text{ or } l, = 1)}{E(\text{lowest excited state with } K, \text{ or } l, = 0)} \quad (6)$$

where E represents the energy of the indicated state measured from the ground state. In this form, γ can be determined for any triatomic molecule.

Since the parameter γ is thus defined for all cases consistently, molecules of various kinds, that is linear, bent or quasilinear, can be plotted along the axis of this parameter; an ideal bent molecule, which has a small rotational constant A and high bending vibrational frequency, falls at $\gamma \approx 0$, and an ideal linear molecule, which can be described by the harmonic approximation of a two-dimensional isotropic oscillator, falls at $\gamma = 1/2$.

Assuming that the uncorrected miscellaneous contribution of the potential anharmonicity to the parameter γ is less than 1%, well behaved linear molecules should fall in the region $\gamma = 0.495$ to 0.505 . Well behaved bent molecules should fall in the region $\gamma = 0$ to 0.01 ; this upper limit for the bent molecule originates from the Born-Oppenheimer approximation, Equation (3).

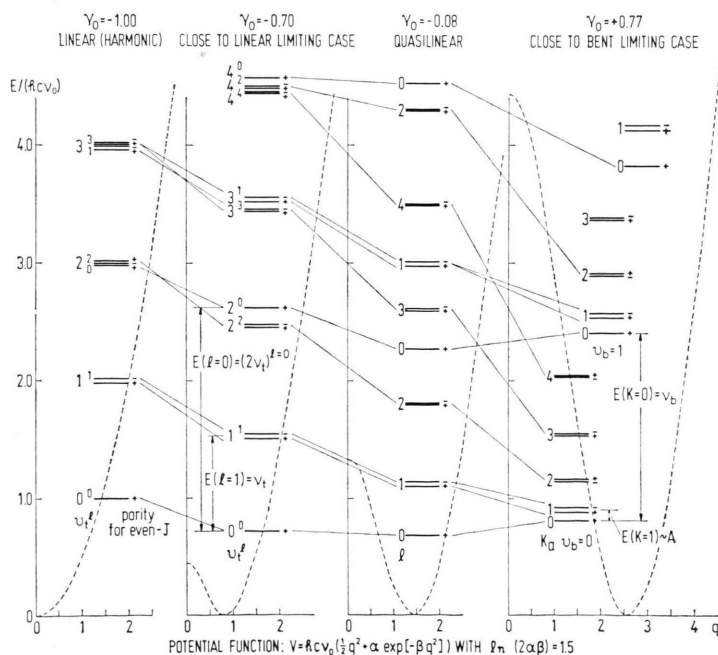


Fig. 1. Correlation diagram of rovibrational energy levels for various degrees of quasilinearity indicated by the value of γ_0 . The l -components of the vibrational levels in the harmonic limiting case ($\gamma_0 = -1.00$) are drawn separately in order to show their rovibrational parity. The energy levels are calculated using a circular minimum potential, and plotted in dimensionless units. One half of the cross section of the potential surface is given by the broken lines for each case.

We have found it to be convenient to use the parameter

$$\gamma_0 = 1 - 4\gamma \quad (7)$$

for display rather than γ itself. In terms of γ_0 the regions mentioned above are as follows:

Molecule	Ideal Molecule	Well Behaved Molecule
linear	$\gamma_0 = -1$	-1.02 to -0.98
bent	$\gamma_0 = +1$	$+1.00$ to 0.96

III. Application of γ

The quantity γ , or γ_0 , has been calculated for a number of triatomic and polyatomic chain molecules. The calculations were done on the basis of the reported constants. Most of the data were taken from Appendix VI of the textbook of Herzberg⁹; otherwise later work was consulted. For obtaining a significant value of γ , it was necessary to remove the effect of accidental resonances from the observed constants. This is especially true for the Fermi resonance in linear triatomic molecules such as the resonance between $2\nu_2$ and ν_1 in CO_2 .

The molecules considered are arranged in Fig. 2 according to the γ_0 values thus obtained. Since most of the molecules investigated can be found in the region of typical (or well behaved) bent molecules, a quadratic scale is used for the γ_0 axis in order to expand the picture near $\gamma_0 = \pm 1.0$.

In the region of positive γ_0 appears the sequence HNNN, HNCO, and HNCS. This sequence of the three molecules corresponds to that of the anomalies found in the observed spectra. As discussed by Neely¹⁰ the hump in the potential function (see Fig. 1), which makes the molecules bent, is smallest for HNCS, while the molecule HNNN is the best behaving bent molecule of this group. Carbon suboxide, which is well known as a quasilinear molecule, is found nearly in the middle of the scale. Fulminic acid is also far from the linear limit. Thus, carbon suboxide, fulminic acid and HNCS can be looked at as truly quasilinear molecules.

It should be mentioned here that the molecule CsOH falls in an extraordinary position beyond the linear limit, though the error estimate is large as indicated by the error bar in Figure 2. This suggests that the potential function of this molecule may be described by a type of negative hump, which will be defined in the next section.

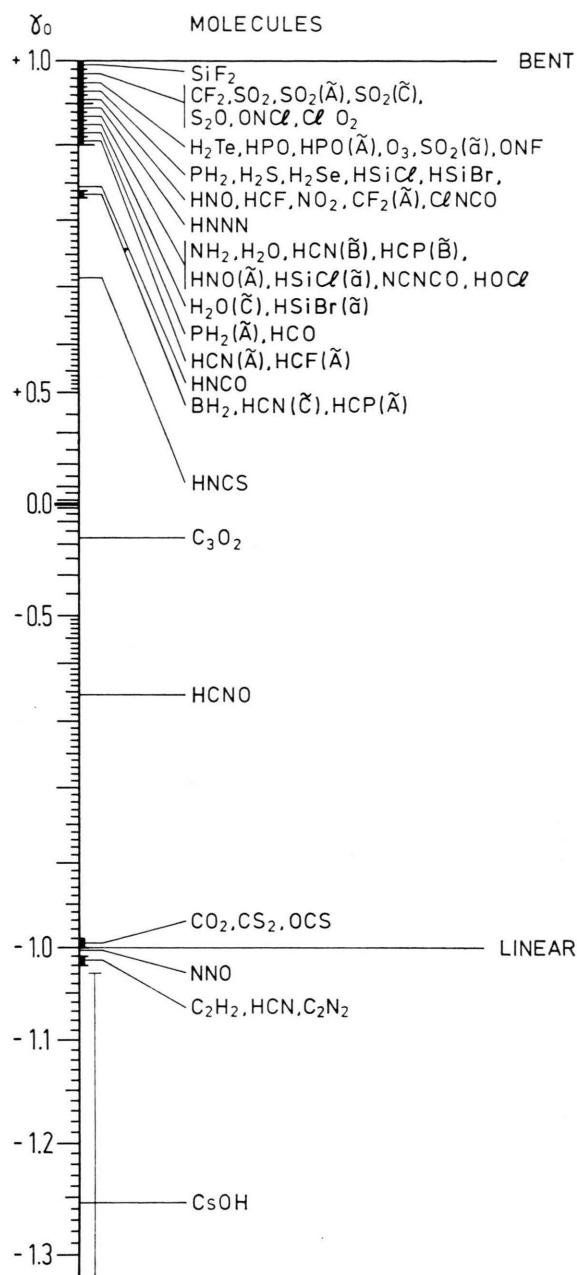


Fig. 2. Molecules are ordered in the sequence of quasilinearity quantified by γ_0 . Recently reported molecular constants were used in evaluating γ_0 for CINCO¹⁴, HNNN¹⁵, NCNCO¹⁴, HOCl¹⁶, HNCO¹⁷, HNCS¹⁸, C_3O_2 ¹⁹, HCNO⁸, CO_2 ²⁰, CS_2 ²¹, OCS²², NNO²³, C_2H_2 ²⁴, HCN²⁵, C_2N_2 ²⁶, and CsOH ²⁷. For the remaining molecules the spectroscopic constants were taken from Herzberg's book⁹. A quadratic scale is used for the γ_0 axis in order to expand the picture near $\gamma_0 = \pm 1.0$. The estimated error of γ_0 for CsOH is indicated by an error bar. The errors for the other molecules are believed to be less than 0.01.

IV. Model Calculations

Calculations of γ , or γ_0 , for various potential functions have been carried out in order to find the relationship between γ and the potential function. The Hamiltonian of the two dimensional isotropic oscillator (harmonic) perturbed by a Gaussian hump was used as the model: the potential function

$$V = h c \nu_0 \{ q^2/2 + \alpha \exp(-\beta q^2) \} \quad (8)$$

was used in the calculation, where ν_0 is the scaling factor for the energy in cm^{-1} and corresponds to the harmonic frequency if the Gaussian hump vanishes, α and β are dimensionless parameters which determine the shape of the potential (β is always taken to be positive in the present work), and q is a dimensionless coordinate which represents displacement from the linear configuration. Sometimes the power series expansion of the potential function,

$$V = h c \nu_0 \{ \frac{1}{2}(1 - 2\alpha\beta)q^2 + \frac{1}{2}\alpha\beta^2q^4 \}, \quad (9)$$

which is obtained from Eq. (8) neglecting the constant term and the higher order terms (higher than q^4) makes it easy to understand the nature of the potential. The effect of the other vibrational modes was neglected (rigid bender model). The change of the reduced mass for the bending vibration due to the large amplitude displacement was also ignored.

The usual slightly anharmonic potential of a linear molecule can be expressed by Eq. (8) or (9) with a harmonic term and a positive or negative quartic term according to the positive or negative α value, respectively. By making the potential hump large enough the potential of a bent molecule can be expressed also by the function of Equation (8). It is recognized that the function of Eq. (8) may not be generally suitable for describing the potential of real molecules. The function was used in the present work because it is convenient for expressing the change of the potential function continuously from the linear to the bent molecular model.

The shape of this potential function, given by Eq. (8), and previously discussed by Dixon² and Shinkle and Coon¹¹, is summarized in Fig. 3 for various molecular models. The discussion is expanded here to negative α values. The form of the potential surface, though not of the spectrum, is indicated uniquely by the product of the potential parameters α and β .

If $\alpha\beta$ is larger than 0.5, the function, Eq. (8), represents a double minimum potential and is ap-

propriate both to a quasilinear and a bent molecule with a negative quadratic and a positive quartic term in Equation (9). For $\alpha\beta > 0.5 \exp(1.5)$, the wall of the hump is steeper than the outside wall of the circular minimum potential surface. Such a potential seems to be unlikely for the bending vibration considered here as discussed by Dixon². Thus the value $0.5 \exp(1.5) \approx 2.2408$ can be considered as the upper limit of the value $\alpha\beta$. If $\alpha\beta$ is at this limit the cubic term of the potential, d^3V/dq^3 , vanishes at the position of the potential minimum.

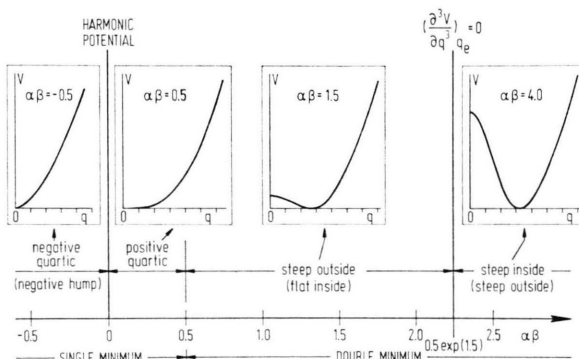


Fig. 3. The shape of the potential function $V = h c \nu_0 \{ q^2/2 + \alpha \exp(-\beta q^2) \}$

is illustrated for various values of the product $\alpha\beta$.

If $0 < \alpha\beta \leq 0.5$, the potential function represents a single minimum potential and corresponds to a linear molecule with a broad bottom potential represented by a positive quadratic and a positive quartic term in Equation (9). If $\alpha\beta = 0$, the potential function reduces to a harmonic one.

If $\alpha\beta < 0$, that is a negative α because we have chosen β positive, the Gaussian hump term in Eq. (8) takes on a negative value. We call this type of potential function a negative hump potential in this paper. The potential in this case represents that of a linear molecule, but with a broad mouth represented by positive quadratic and negative quartic terms in Equation (9).

Though the value of $\alpha\beta$ indicates the shape of the potential surface, it is not sufficient to indicate the quasilinearity. This may be understood by considering the case $\alpha\beta > 0.5$. The height of the potential hump B measured from the potential minimum and the dimensionless equilibrium coordinate q_e of

the bending vibration are given in Ref. ¹¹ as

$$B = (2\alpha\beta - \varrho - 1)/(2\beta), \quad (10)$$

and

$$q_e^2 = \varrho/\beta \quad (11)$$

where $\varrho = \ln(2\alpha\beta)$, and α and β are the parameters in Equation (8). The ratio B/q_e^2 is a function of $\alpha\beta$ only. Thus a distinctly bent molecule with high potential hump can be represented by the same $\alpha\beta$ as a slightly bent molecule with a low potential hump

The parameter γ , which is a ratio between energy intervals, does not depend on the constant ν_0 in Eq. (8), since ν_0 is a scaling factor. The parameter γ is thus a function of α and β . The calculated γ_0 are plotted against α for various values of $\alpha\beta$ in Figure 4.

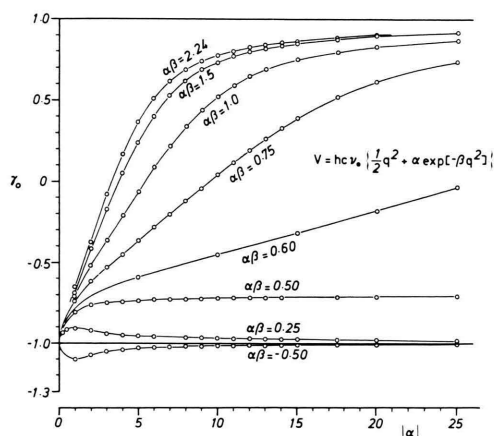


Fig. 4. Calculated values of γ_0 are plotted against the absolute value of the parameter α for various values of the product $\alpha\beta$.

If the potential parameter α is negative, giving a negative hump, γ_0 is smaller than -1 . If $0 < \alpha\beta \leq 0.5$, it seems that the value of γ_0 can not overcome the upper limit of about -0.7 . It appears indeed that γ_0 approaches the linear limit -1 for large α in the curves for small $\alpha\beta$. In other words, when the value of γ_0 is larger than -0.7 , the potential should have a hump at the linear conformation. If $\alpha\beta > 0.5$, the γ_0 value approaches the bent limit for large α . This approach is more rapid for the larger values of $\alpha\beta$. The γ_0 curves for various $\alpha\beta$ values are converging in the region of $\alpha\beta \approx 0.5 \exp(1.5)$. For $\alpha\beta > 0.5 \exp(1.5)$, the

curves turn around and make a head in Figure 4. The $\alpha\beta$ value at the turning point varies with α .

As can be seen from Fig. 4, we can not determine the potential parameters α and β simultaneously from the γ value. In Fig. 5, three different potentials are illustrated which give the same γ_0 value ($\gamma_0 = 0.614$). Additional information from rotational or vibrational excited states is necessary to determine the potential.

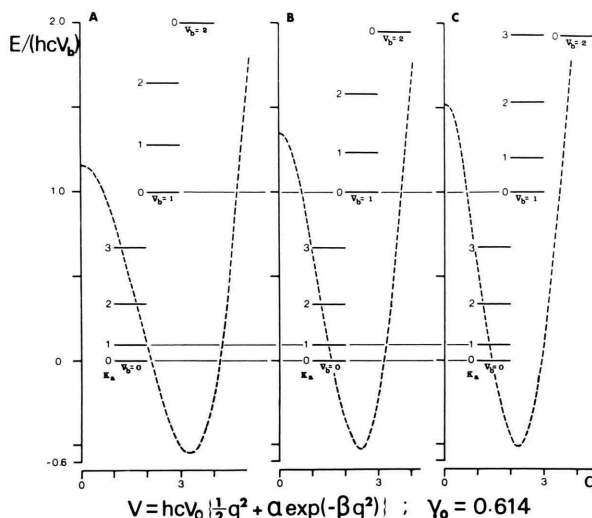


Fig. 5. Three different potential curves are illustrated which give a common γ_0 value of 0.614. The vibrational energy difference between $v_b=0$ and 1 is normalized to 1 for each case. The potential parameters for cases A, B, and C are, ($\alpha=20.0$, $\alpha\beta=0.75$), ($\alpha=8.0$, $\alpha\beta=1.5$), and ($\alpha=7.0$, $\alpha\beta=2.2408$), respectively.

V. Discussion

It is useful to define the following two parameters for exploring further the physical meaning of the quantity γ_0 , or γ :

$$\gamma_B = (1 - \gamma_0)/4$$

and

$$\gamma_L = (1 + \gamma_0)/4. \quad (12)$$

Then γ_B and γ_L are very small quantities for the bent and linear limiting cases, respectively. Though γ_B is identical to γ in Eq. (6), we put the suffix B on it here for the symmetry of the definitions.

The quantity γ_B has an exact physical meaning; it is equivalent to the square of the Born-Oppen-

heimer constant α . Since the terms in the molecular energy can be classified by their order of magnitude, which is represented by α^2 , it is also possible to express the molecular constants by a power series in γ_B for a bent molecule. If only the bending vibration and rotation about the axis of least moment of inertia are taken into account, we obtain

$$\begin{aligned} \alpha_A &= -6 A \gamma_B, \\ D_K &= 4 A \gamma_B^2, \\ H_K &= 48 A \gamma_B^4, \text{ etc.,} \end{aligned} \quad (13)$$

where α_A , D_K , and H_K are the vibration-rotation interaction constant, the quartic and the sextic centrifugal distortion constants, respectively, by analogy with a diatomic molecule¹² as discussed by Polo¹³, neglecting the anharmonicity of the potential and higher order contributions. The contribution of the potential anharmonicity to the centrifugal distortion constants in the ground vibrational state is, at the most, in the order of γ_B^4 . On the other hand, their contribution to α_A is in the order of γ_B . It can be seen in Fig. 5 that, if the notation of bent molecules is used, the levels for the excited vibrational states have more information for determining the potential function than the K -rotational levels in the ground vibrational state.

On the other hand, from Eqs. (5), (7), and (12) we obtain for linear molecules

$$\gamma_L \approx (x_{tt} - g_{tt}) / (2 \omega_t + 8 x_{tt}) \quad (14)$$

where ω_t is the harmonic frequency of the bending vibration and x_{tt} and g_{tt} are the anharmonicity constants associated with the bending vibration. Neglecting all other vibrations, we obtain from vibra-

tion-rotation theory²⁸

$$x_{tt} = \frac{3}{2} k_{tttt},$$

and

$$g_{tt} = -\frac{1}{2} k_{tttt}. \quad (15)$$

where k_{tttt} is the quartic force constant for the bending vibration. Then, ignoring the small term in the denominator of Eq. (14), we obtain

$$\gamma_L = k_{tttt} / \omega_t. \quad (16)$$

The quantity γ_L represents the magnitude of the potential anharmonicity for the degenerate bending vibration in a linear molecular model.

Although the parameter γ_0 has been defined on the basis of a simple consideration of the correlation diagram and the separation of variables, the quantity γ_0 is related to the conventional molecular parameters in both the linear and bent limiting cases. γ_B or γ_L can be considered as a measure of the perturbation in the Hamiltonian of a molecule which is close to the bent or linear limiting cases, respectively.

For molecules for which γ_0 is far from the $+1$ or -1 , we have found the parameter γ_0 itself to be the most convenient quantity for defining the degree of quasilinearity. With this "quasilinearity parameter" it is possible to classify and compare the most disparate members of the family of chainform molecules.

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