

# LINEAR OR QUASI-LINEAR

## – THAT IS THE QUESTION

Tsuneo Hirano, Department of Chemistry, Faculty of Science, Ochanomizu University, 2-1-1 Otsuka, Bunkyo-ku, Tokyo 112-8610, Japan

Umpei Nagashima, Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

Valerie Derpmann and Per Jensen, Physikalische und Theoretische Chemie, Bergische Universität, D-42097 Wuppertal, Germany



### Introduction

When spectroscopists determine the bond lengths of linear triatomic molecules from experimentally derived  $B_0$  values, they sometimes obtain values much too short to be in keeping with chemical common sense. This is often said to be "because the molecule is quasi-linear". In most cases, however, this statement is not based on firm knowledge of the bending potential responsible for the shorter bond lengths. Since the average structure of any triatomic molecule is bent (with the averaging being done over the ro-vibrational wavefunction), quasi-linear behavior is common to all molecules, even for those with linear equilibrium structures. In this sense, there is no linear molecule.

Although this is true, there is a more rigorous definition of "linear" and "quasi-linear." We can classify the molecule as being linear when the bending potential energy function has its minimum at a linear structure, and as quasi-linear when potential energy function has a barrier at linearity whose height is comparable to the zero-point bending vibrational energy. We discuss here "linearity" and "quasi-linearity" from this point of view.

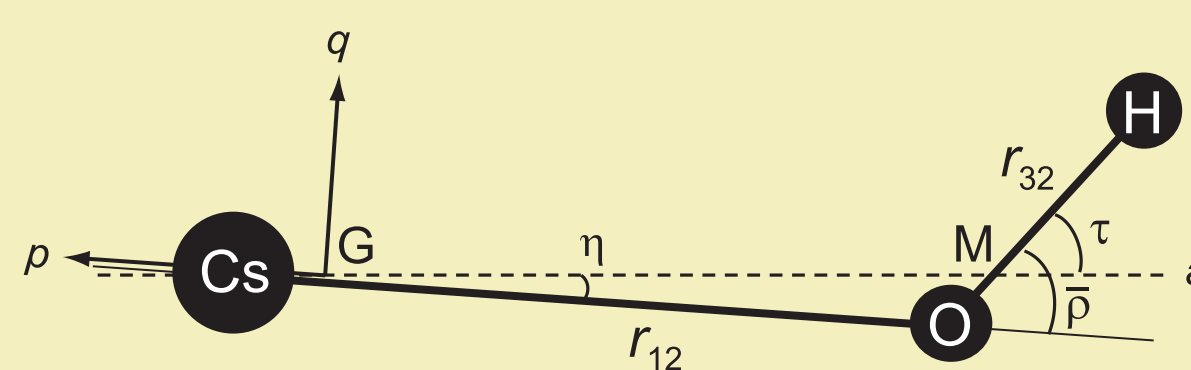
In computational molecular spectroscopy, it is easy to distinguish "linear" and "quasi-linear" molecules since we start from the calculation of the potential energy surface and determine directly the equilibrium structure. However, in experimental spectroscopy, to obtain the information on the potential energy surface it is necessary to assign and analyze successfully, in terms of a model, (many) observed spectral lines. If an unsatisfactory model is used for the analysis the resulting information on the bending potential energy surface becomes incorrect. Ideally, the experimentalists need a procedure to determine the shape of the potential energy surface at an early stage of their analyses.

For many "linear" molecules, such as  $\tilde{X}^1\Sigma^+$  and  $\tilde{A}^1\Sigma^+$  state MgNC/MgCN [1,2],  $\tilde{X}^6\Delta$  FeNC [3],  $\tilde{X}^6\Delta$  FeCN [4],  $\tilde{X}^3\Phi$  CoCN [5],  $\tilde{X}^2\Pi$  BrCN [6], and  $\tilde{X}^1\Sigma^+$  CsOH [7], we have carried out *ab initio* calculations of the potential energy surfaces combined with variational solutions of the rotation-vibration Schrödinger equation. In the same manner, we have studied the "quasi-linear" molecule  $\tilde{X}^6A'$  FeOH [8,9]. As an example of a linear molecule we discuss in detail  $\tilde{X}^1\Sigma^+$  CsOH [7], and as an example of a quasi-linear molecule we discuss  $\tilde{X}^6A'$  FeOH [8,9].

1. T. Hirano, K. Ishii, T. E. Odaka, and P. Jensen, *J. Mol. Spectrosc.* **215**, 42-57 (2002).
2. T. E. Odaka, T. Hirano, and P. Jensen, *J. Mol. Spectrosc.* **211**, 147-161 (2002).
3. T. Hirano, R. Okuda, U. Nagashima, V. Špirko, and P. Jensen, *J. Mol. Spectrosc.* **236**, 234-247 (2006).
4. T. Hirano, M. Amano, Y. Mitsui, S. S. Itono, R. Okuda, U. Nagashima, and P. Jensen, *J. Mol. Spectrosc.* **243**, 267-279 (2007).
5. T. Hirano, R. Okuda, U. Nagashima, and P. Jensen, *Mol. Phys.* **105**, 599-611 (2007).
6. T. Hirano, R. Okuda, U. Nagashima, Y. Nakashima, K. Tanaka, and P. Jensen, *J. Mol. Spectrosc.* **243**, 202-218 (2007).
7. T. Hirano, V. Derpmann, U. Nagashima, and P. Jensen, *J. Mol. Spectrosc.*, in press.
8. T. Hirano, P. R. Bunker, S. Patchkovskii, U. Nagashima, and P. Jensen, *J. Mol. Spectrosc.* **256**, 45-52 (2009).
9. T. Hirano, U. Nagashima, G. Winnewisser, and P. Jensen, *J. Chem. Phys.* **132**, 094303/1-10 (2010).

### Averaged geometries

Coordinates and axis systems used to describe CsOH and FeOH



Vibrationally averaged structural parameters for CsOH, CsOD, FeOH, and FeOD are obtained by averaging over the rovibrational wavefunctions from a MORBID calculation.

$\langle \bar{\rho} \rangle = \langle \Phi_{\text{vib}}^{\text{vib}} | \bar{\rho} | \Phi_{\text{vib}}^{\text{vib}} \rangle$  with  $n = 1$  or 2 and  $\Phi_{\text{vib}}^{\text{vib}}$  as the normalized bending basis wavefunction with the largest contribution to the vibrational state in question. The quantum mechanical uncertainty of  $\langle \bar{\rho} \rangle$  is  $\delta \bar{\rho} = (\langle \bar{\rho}^2 \rangle - \langle \bar{\rho} \rangle^2)^{1/2}$ .

Bond lengths in Å				
	$r_0(\text{Cs-O})$	$r_0(\text{O-H})$	$r_0(\text{Cs-O})$	$r_0(\text{O-H})$
CsOH	Lide <i>et al.</i> <sup>a)</sup>	2.391(2) <sup>b)</sup>	0.960(10) <sup>b)</sup>	2.395
	Conventional method		2.403	0.969
	CCSD(T)_DK3		2.4231	0.9742
	MORBID		2.4227	0.9206
	a-axis projection			
FeOH	MR-SDCI+Q+ $E_{\text{rel}}^6A'$ ( $\Delta$ )	1.8059	0.9520	1.8049
	MORBID			1.8045
	a-axis projection			0.9669
				0.7320

<sup>a)</sup> D.R. Lide, Jr., and R.L. Kuczkowski, *J. Chem. Phys.*, **46**, 4768 (1967).  
<sup>b)</sup> D.R. Lide, Jr., and C. Matsumura, *J. Chem. Phys.*, **50**, 3080 (1969).  
<sup>c)</sup>  $r_0$  values

### CsOH

State	$E_{\text{vib}}/\text{cm}^{-1}$	$B_0/\text{cm}^{-1}$	$r_0/\text{Å}$	$r_0/\text{Å}$	$r_0 \cos \eta/\text{Å}$	$r_0 \cos \eta/\text{Å}$	$\langle \bar{\rho} \rangle / \langle \delta \bar{\rho} \rangle / \text{deg}$
g.s.	0.0	0.18436	2.3887	0.9754	2.3882	0.9246	17(9)
$v_2^1$	362.0	0.18311	2.4108	0.9775	2.4106	0.8764	26(9)
$v_3^1$	380.0	0.18323	2.4100	0.9754	2.4086	0.8242	17(9)
$2v_2^0$	699.1	0.18345	2.4120	0.9778	2.4115	0.8270	30(15)
$v_2^1+v_3^1$	739.0	0.18200	2.4223	0.9775	2.4222	0.8761	26(9)
$2v_3^0$	757.4	0.18210	2.4215	0.9754	2.4211	0.8238	17(9)
$v_2^1$	3691.0	0.18408	2.3983	1.0085	2.3979	0.8520	17(9)

### CsOD

State	$E_{\text{vib}}/\text{cm}^{-1}$	$B_0/\text{cm}^{-1}$	$r_0/\text{Å}$	$r_0/\text{Å}$	$r_0 \cos \eta/\text{Å}$	$r_0 \cos \eta/\text{Å}$	$\langle \bar{\rho} \rangle / \langle \delta \bar{\rho} \rangle / \text{deg}$
g.s.	0.0	0.16726	2.3881	0.9707	2.3874	0.9349	14(8)
$v_2^1$	275.2	0.16667	2.4075	0.9723	2.4071	0.9005	22(8)
$v_3^1$	373.6	0.16629	2.4090	0.9708	2.4083	0.9348	14(8)
$2v_2^0$	529.8	0.16725	2.4086	0.9725	2.4076	0.8615	26(13)
$v_2^1+v_3^1$	646.2	0.16569	2.4185	0.9723	2.4182	0.9003	22(8)
$2v_3^0$	743.1	0.16532	2.4201	0.9708	2.4194	0.9346	14(8)
$v_2^1$	2721.5	0.16696	2.3978	0.9947	2.3971	0.9554	14(8)

### FeOH

$(v_2, v_3)^{\text{vib}}$	$(v_2^{\text{vib}})^{\text{vib}}$	$E_{\text{vib}}/\text{cm}^{-1}$	$r_0/\text{Å}$	$r_0/\text{Å}$	$r_0 \cos \eta/\text{Å}$	$r_0 \cos \eta/\text{Å}$	$\langle \bar{\rho} \rangle / \langle \delta \bar{\rho} \rangle / \text{deg}$
(0,0) <sup>0</sup>	0 <sup>0</sup>	0.0	1.8049	0.9669	1.8045	0.7320	39(14)
(0,0) <sup>1</sup>	1 <sup>1</sup>	72.8	1.8094	0.9684	1.8090	0.6881	43(12)
(0,1) <sup>0</sup>	2 <sup>0</sup>	323.4	1.8025	0.9675	1.8020	0.7439	35(22)
(0,1) <sup>1</sup>	3 <sup>1</sup>	504.5	1.8095	0.9702	1.8091	0.6779	43(20)
(2,0) <sup>0</sup>	4 <sup>0</sup>	753.1	1.8090	0.9707	1.8083	0.6691	42(25)
(2,0) <sup>1</sup>	5 <sup>1</sup>	1012.0	1.8137	0.9732	1.8132	0.6310	46(24)
(3,0) <sup>0</sup>	6 <sup>0</sup>	1230.6	1.8145	0.9737	1.8138	0.6138	47(28)
(3,0) <sup>1</sup>	7 <sup>1</sup>	1595.6	1.8185	0.9762	1.8179	0.5859	50(26)
(1,0,0) <sup>0</sup>	0 <sup>0</sup>	3831.6	1.8062	0.9687	1.8058	0.7240	39(14)
(1,0,0) <sup>1</sup>	1 <sup>1</sup>	3890.1	1.8092	0.9677	1.8087	0.6880	43(12)
(0,1,1) <sup>0</sup>	0 <sup>0</sup>	709.2	1.8163	0.9674	1.8150	0.7201	39(14)
(0,1,1) <sup>1</sup>	1 <sup>1</sup>	775.9	1.8194	0.9687	1.8189	0.6785	43(12)

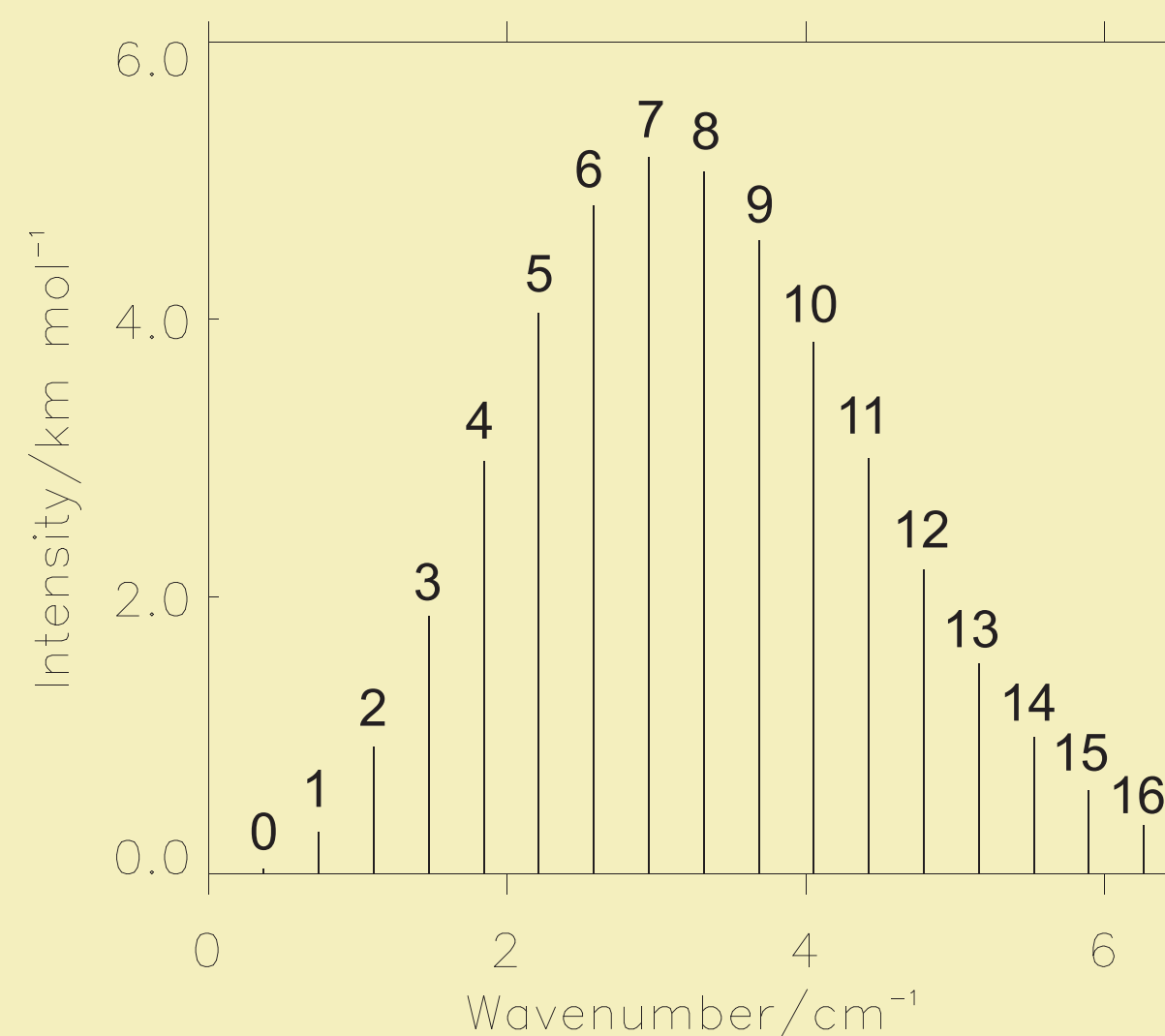
### FeOD

$(v_2, v_3)^{\text{vib}}$	$(v_2^{\text{vib}})^{\text{vib}}$	$E_{\text{vib}}/\text{cm}^{-1}$	$r_0/\text{Å}$	$r_0/\text{Å}$	$r_0 \cos \eta/\text{Å}$	$r_0 \cos \eta/\text{Å}$	$\langle \bar{\rho} \rangle / \langle \delta \bar{\rho} \rangle / \text{deg}$
(0,0) <sup>0</sup>	0 <sup>0</sup>	0.0	1.8060	0.9628	1.8048	0.7327	40(12)
(0,0) <sup>1</sup>	1 <sup>1</sup>	36.8	1.8099	0.9631	1.8094	0.7045	43(11)
(0,1) <sup>0</sup>	2 <sup>0</sup>	229.6	1.8006	0.9622	1.7994	0.7749	33(20)
(0,1) <sup>1</sup>	3 <sup>1</sup>	331.6	1.8072	0.9644	1.8059	0.7147	41(18)
(2,0) <sup>0</sup>	4 <sup>0</sup>	501.1	1.8056	0.9645	1.8041	0.7172	38(23)
(2,0) <sup>1</sup>	5 <sup>1</sup>	663.8	1.8102	0.9665	1.8088	0.6801	43(22)
(3,0) <sup>0</sup>	6 <sup>0</sup>	849.7	1.8100	0.9668	1.8093	0.6711	43(25)
(3,0) <sup>1</sup>	7 <sup>1</sup>	1058.2	1.8138	0.9683	1.8123	0.6497	46(24)
(1,0,0) <sup>0</sup>	0 <sup>0</sup>	2815.9	1.8072	0.9662	1.8058	0.7245	40(12)
(1,0,0) <sup>1</sup>	1 <sup>1</sup>	2846.5	1.8090	0.9668	1.8075	0.7047	43(11)
(0,1,1) <sup>0</sup>	0 <sup>0</sup>	684.7	1.8167	0.9633	1.8153	0.7228	40(12)
(0,1,1) <sup>1</sup>	1 <sup>1</sup>	720.0	1.8168	0.9640	1.8173	0.7008	43(11)

### Rotational spectra

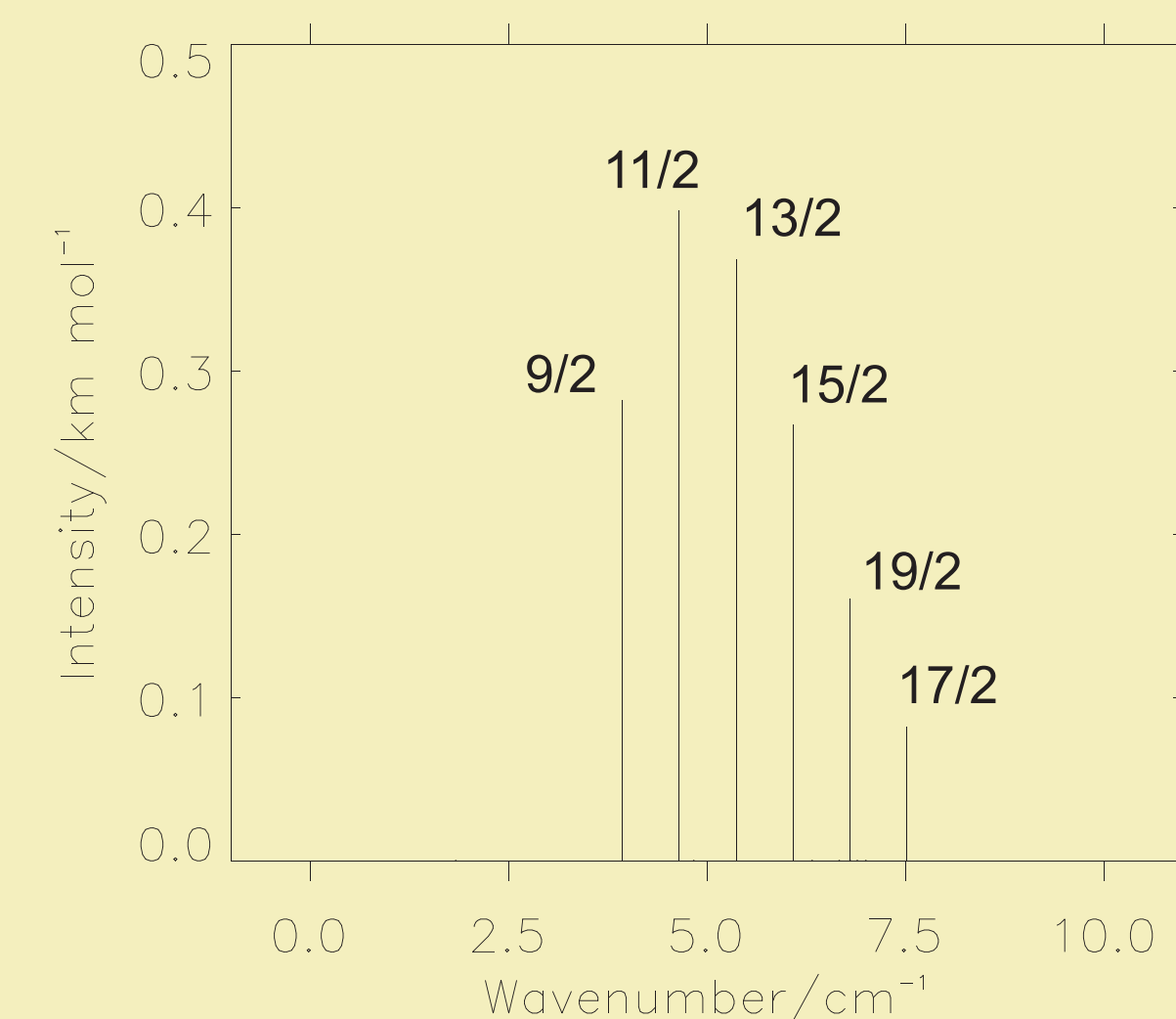
#### CsOH

The rotational spectrum of  $\tilde{X}^1\Sigma^+$  CsOH, simulated *ab initio* at an absolute temperature of  $T = 12$  K. The  $J$  values of the initial states of the transitions are indicated.

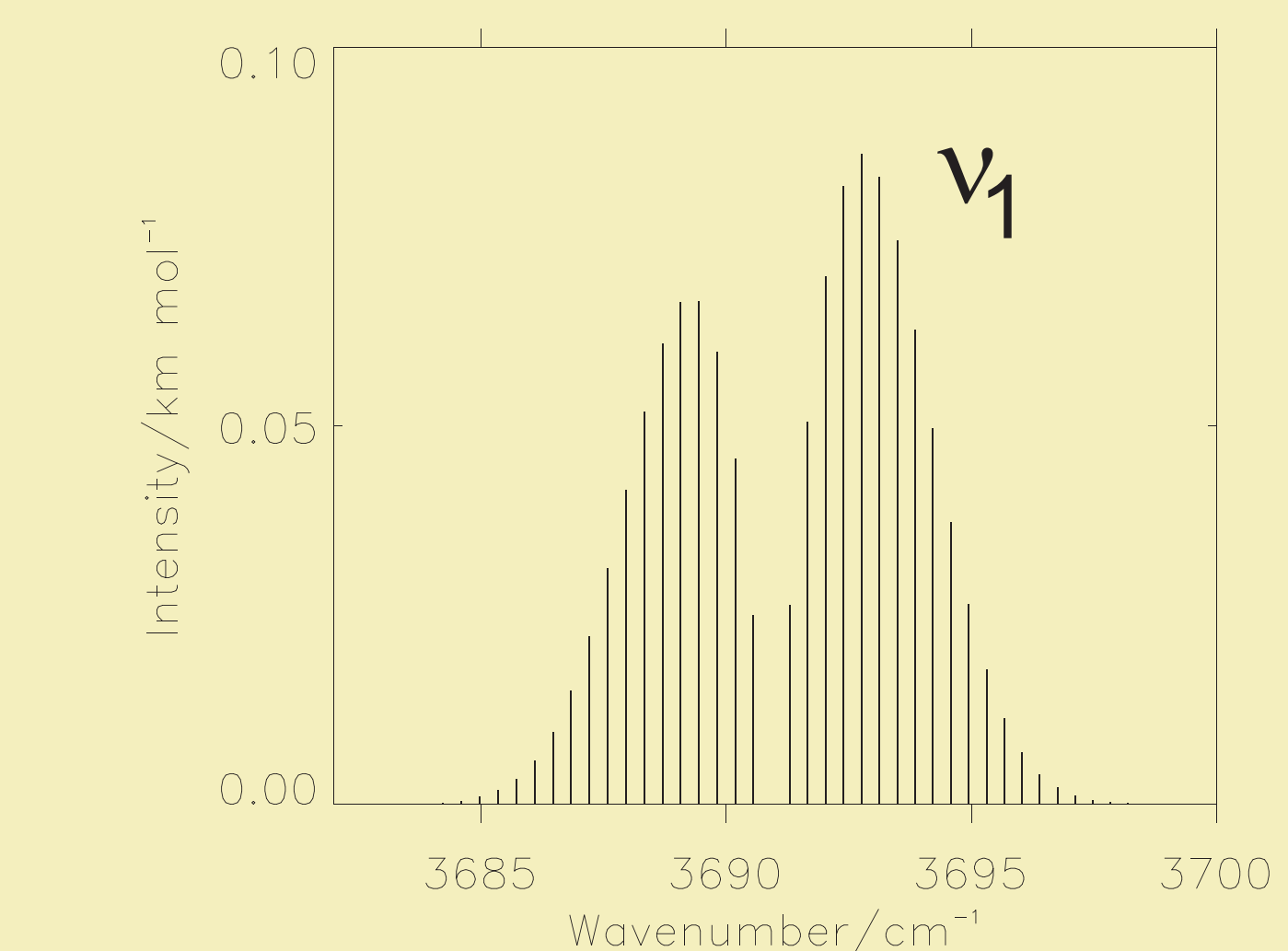
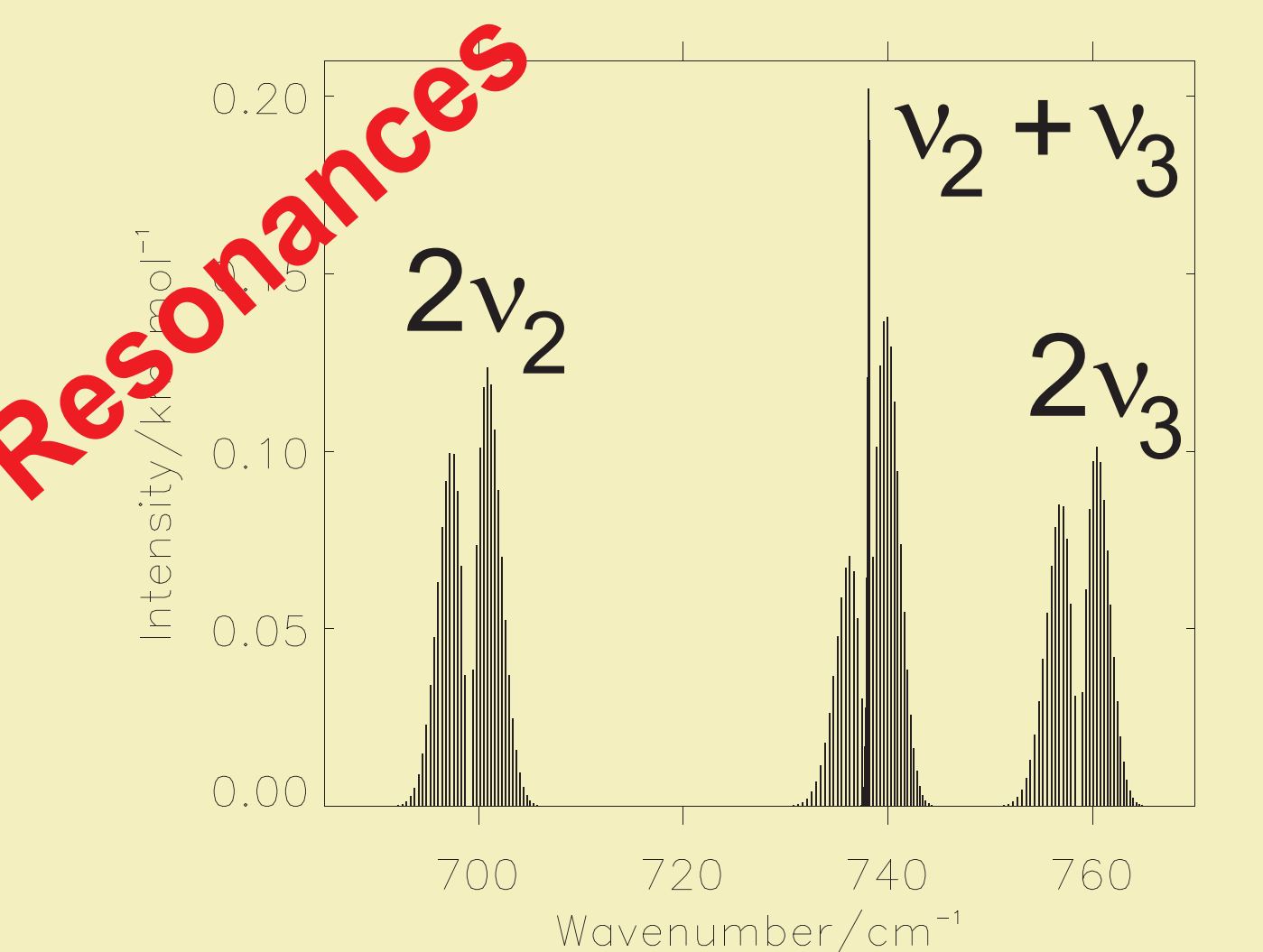
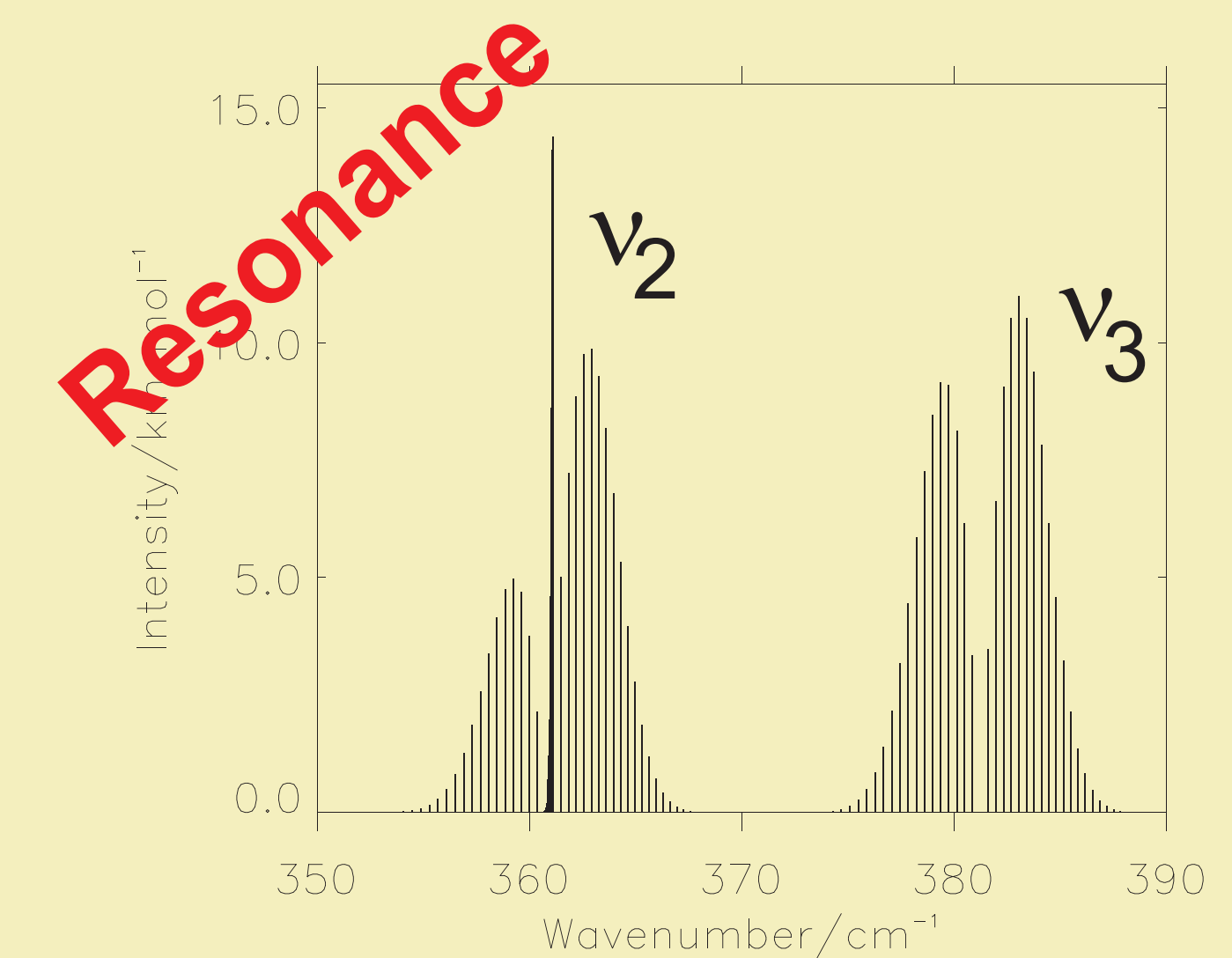


#### FeOH

The rotational spectrum of  $\tilde{X}^6A'$  FeOH, simulated *ab initio* at an absolute temperature of  $T = 10$  K [T. Hirano, P. R. Bunker, S. Patchkovskii, U. Nagashima, and P. Jensen, *J. Mol. Spectrosc.* **256**, 45-52 (2009)]. The  $J$  values of the initial states of the transitions are indicated.



### CsOH rotation-vibration spectra

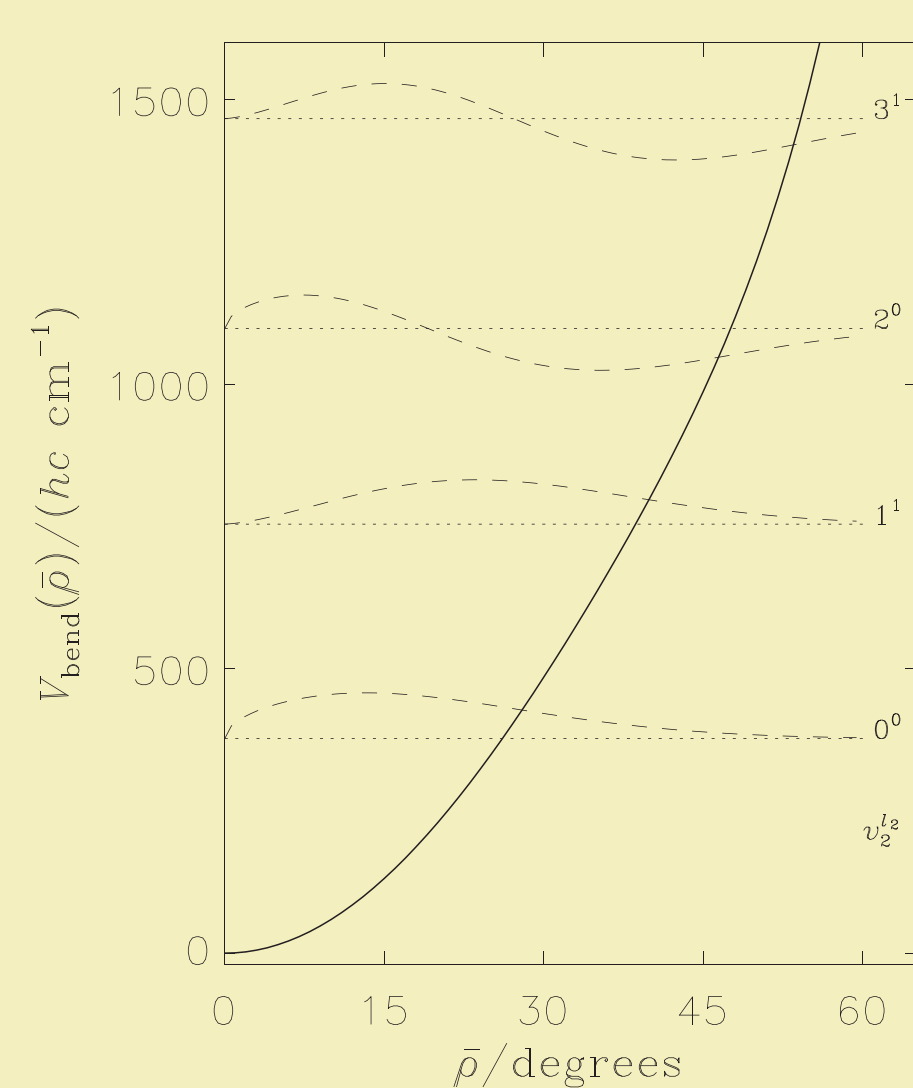


Spectra simulated *ab initio* at  $T = 12$  K

### Bending potentials

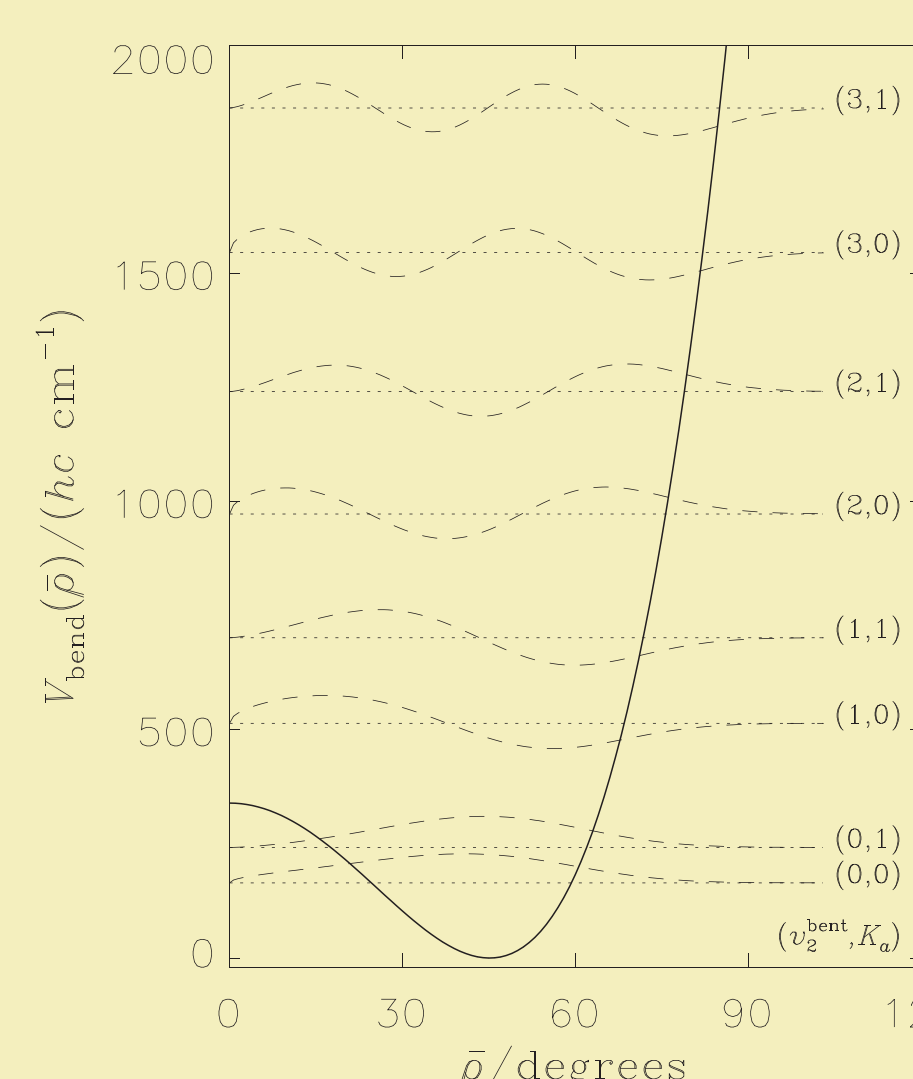
#### CsOH

A classical molecule with a very floppy, large-amplitude bending motion. Its rotational spectrum was studied by Lide and co-workers more than 40 years ago [D.R. Lide Jr., R.L. Kuczkowski, *J. Chem. Phys.* **46**, 4768-4774 (1967); C. Matsumura, D.R. Lide Jr., *J. Chem. Phys.* **50**, 71-75 (1969); D.R. Lide Jr., C. Matsumura, *J. Chem. Phys.* **50**, 3080-3086 (1969)] but no infrared spectra are available. The bending amplitude is so large that  $B_0$  shows an "unusual variation" with  $v_2$  as the bending mode is excited, and although Lide and co-workers assumed a linear equilibrium structure, they could not definitely conclude in the end that CsOH is a linear molecule. We show here the bending potential curve, calculated at the RCCSD(T)\_DK3[QZP +  $g$  ANO-RCC (Cs, O, H)] level of theory, with the lowest bending energy levels and wavefunctions indicated. Apparently CsOH is a linear molecule, but the bending potential is very shallow....



#### FeOH

For FeOH, no experimental spectroscopic data are available but we have recently carried out first-principles simulations of the spectra [T. Hirano, P. R. Bunker, S. Patchkovskii, U. Nagashima, and P. Jensen, *J. Mol. Spectrosc.* **256**, 45-52 (2009); T. Hirano, U. Nagashima, G. Winnewisser, and P. Jensen, *J. Chem. Phys.* **132**, 094303/1-10 (2010)]. The potential energy surface is calculated *ab initio* at the MR-SDCI+Q+ $E_{\text{rel}}$  [Roo's ANO (Fe), aug-cc-pVQZ (O, H)] level of theory. The bending potential energy curve has a small barrier to linearity and the pattern of bending energies reflects this....



The low-temperature rotational spectra of  $\tilde{X}^1\Sigma^+$  CsOH and  $\tilde{X}^6A'$  FeOH are both progressions of nearly-equidistant transitions; we cannot use these spectra to determine whether the molecules are linear or quasi-linear.

### Yamada-Winnewisser quasi-linearity parameter

$$\gamma_0 = 1 - 4 \times \frac{E(v_2 = |l_2| = 1) - E(v_2 = |l_2| = 0)}{E(v_2 = 2, |l_2| = 0) - E(v_2 = |l_2| = 0)}$$

K. Yamada and M. Winnewisser, *Z. Naturforsch.* **31a**, 139-144 (1976).

Linear	$\gamma_0 = -1$
Quasi-linear	$\gamma_0 = 0$
Strongly bent	$\gamma_0 = +1$

If it is possible to derive from experiment the energy values necessary to determine  $\gamma_0$ , then the molecule in question can be classified as linear, quasi-linear, or bent at an early stage of the analysis.

		$\langle \bar{\rho} \rangle / \langle \delta \bar{\rho} \rangle / \text{deg}$	
Linear	$^3\Phi$ CoCN	8°(5°)	$\gamma_0 = -1$
	$^2\Delta$ NiCN	9°(5°)	
	$^6\Delta$ FeCN	10°(5°)	
	$^6\Delta$ FeNC	13°(7°)	
	$^1\Sigma$ CsOH	17°(9°)	
Quasi-linear	$^6\Delta$ FeOH	39°(14°)	$\gamma_0 = 0.1$