

## Rotational $\ell$ -type resonance in BeH<sub>2</sub>, BeD<sub>2</sub>, and MgH<sub>2</sub>

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In two previous papers on the infrared emission spectra of gaseous BeH<sub>2</sub>, BeD<sub>2</sub>, and MgH<sub>2</sub> molecules, we reported rotational analyses of the antisymmetric stretching fundamental band and several hot bands.<sup>1,2</sup> A customary effective rotational energy level expression, which is a power series in  $J(J+1)$  with  $B_{[v]}$ ,  $D_{[v]}$ , and  $H_{[v]}$  constants, was used for most of the observed vibrational levels. For all the vibrational levels with  $v_2=2$ , we observed large splittings between the  $e$  and  $f$  parity components of the  $\Delta$  states, i.e.,  $02^20(\Delta_g)$ ,  $02^21(\Delta_u)$ , and  $02^22(\Delta_g)$  states. These splittings were attributed to rotational  $\ell$ -type resonances between these  $\Delta$  states and the associated nearby  $\Sigma^+$  states,  $02^00(\Sigma_g^+)$ ,  $02^01(\Sigma_u^+)$ , and  $02^02(\Sigma_g^+)$ , respectively. Since all the rotational levels of a  $\Sigma^+$  state have  $e$  parity, they interact only with the  $e$  parity component of the nearby  $\Delta$  state, and thus the  $\Delta(f)$  levels are not perturbed. Following Maki and Lide who analyzed rotational  $\ell$ -type resonances for HCN,<sup>3</sup> we used a  $2 \times 2$  Hamiltonian matrix for the  $e$  levels, while the rotational energy expression for the  $f$  levels was the customary power series in  $J(J+1)$ . However, only for the BeD<sub>2</sub> molecule we could obtain a satisfactory fit to the observed transitions. For BeH<sub>2</sub>, fitting errors of about  $0.08 \text{ cm}^{-1}$  were found for lines of the  $02^21(\Delta_u) \rightarrow 02^20(\Delta_g)$  and the  $02^22(\Delta_g) \rightarrow 02^21(\Delta_u)$  bands,<sup>1</sup> and were assumed to be due to further perturbations of the  $02^21(\Delta_u)$  state by the nearby  $05^30(\Phi_u)$  state. Although similar perturbations do not exist in MgH<sub>2</sub>, a satisfactory  $\ell$ -type resonance fit could not be obtained for this molecule, and only lines from the  $f$  parity component of the  $\Delta$  states were fitted. The problems in the  $\ell$ -type resonance fits of BeH<sub>2</sub> and MgH<sub>2</sub> have now been resolved, and the results are reported in this Note.

There is an  $\ell$ -dependent term in the vibrational energy level expression for symmetric linear triatomic molecules, i.e.,  $g_{22}\ell^2$ . The theoretical calculations of Martin and Lee<sup>4</sup> for BeH<sub>2</sub> had predicted the  $g_{22}$  constant to be  $+2.46 \text{ cm}^{-1}$ , which means that for a vibrational level with  $v_2=2$  the vibrational energy of the  $\Delta$  state ( $\ell=2$ ) is larger than that of the  $\Sigma^+$  state ( $\ell=0$ ) by  $4g_{22}$ . In our previous paper on BeH<sub>2</sub> and BeD<sub>2</sub>,<sup>1</sup> the rotational energy had been expressed as a power series in  $J(J+1)$ , and it was assumed that the rotational levels of the  $02^20(\Delta_g)$  state lie higher in energy compared with those of the  $02^00(\Sigma_g^+)$  state because of the positive  $g_{22}$  value. The common method for assigning any  $\Sigma^+$  or  $\Delta$  state is based on the first observed line in each branch, since  $J=0$  and  $1$  do not exist in  $\Delta$  states. However, when spectra are congested because of overlapping bands, it can be difficult to ascertain which lines are missing. We have now realized that our previous assignments of the  $\Sigma^+(e)$  and  $\Delta(e)$  components should

be switched for BeH<sub>2</sub>. When the rotational energy is expressed as a power series in  $[J(J+1)-\ell^2]$  instead of  $J(J+1)$ ,<sup>5</sup> the  $\Sigma^+$  state ( $\ell=0$ ) has a larger rotational energy compared with the  $\Delta$  state ( $\ell=2$ ) for each value of  $J$ , and the difference is approximately equal to  $4B$ . Therefore, in order to locate the relative positions of the  $\Delta$  and  $\Sigma^+$  state rotational levels for each value of  $J$ , the sign of  $[g_{22}-B]$  should be considered, because the  $\ell$  dependence of the total energy level expression is now  $[g_{22}-B]\ell^2$ .

For BeH<sub>2</sub>, the  $B$  constant ( $\sim 4.72 \text{ cm}^{-1}$ ) is larger than  $g_{22}$ , so the  $\Sigma^+$  state rotational levels lie higher than those of the  $\Delta$  state. New  $\ell$ -type resonance fits have been performed for the  $02^21(\Delta_u) \rightarrow 02^20(\Delta_g)$ ,  $02^01(\Sigma_u^+) \rightarrow 02^00(\Sigma_g^+)$ ,  $02^22(\Delta_g) \rightarrow 02^21(\Delta_u)$ , and  $02^02(\Sigma_g^+) \rightarrow 02^01(\Sigma_u^+)$  bands of BeH<sub>2</sub>, using a power series in  $[J(J+1)-\ell^2]$  for the rotational energy, and we were able to fit all the observed transitions within their experimental uncertainty of  $0.002 \text{ cm}^{-1}$ . The  $2 \times 2$  Hamiltonian matrix used for the  $\Sigma^+(e)$  and  $\Delta(e)$  levels and the associated matrix elements are given in the following equations in which  $x=J(J+1)$ :

$$H = \begin{pmatrix} E_{\Delta}^0 & \sqrt{2}W_{20} \\ \sqrt{2}W_{20} & E_{\Sigma}^0 \end{pmatrix}, \quad (1)$$

$$E_{\Delta}^0 = G_{\Delta} + B_{\Delta}(x-4) - D_{\Delta}(x-4)^2 + H_{\Delta}(x-4)^3, \quad (2)$$

$$E_{\Sigma}^0 = (G_{\Delta} - 4g_{22}) + B_{\Sigma}x - D_{\Sigma}x^2 + H_{\Sigma}x^3, \quad (3)$$

$$W_{20} = \frac{1}{\sqrt{2}}(q + q_Dx + q_Hx^2)\sqrt{x(x-2)}, \quad (4)$$

and the energy expression for the  $\Delta(f)$  levels is exactly the same as Eq. (2). The new constants for BeH<sub>2</sub> are presented in Table I. Similarly, we were able to obtain a good fit to all the observed transitions of MgH<sub>2</sub>, i.e., the  $02^21(\Delta_u) \rightarrow 02^20(\Delta_g)$  and  $02^01(\Sigma_u^+) \rightarrow 02^00(\Sigma_g^+)$  bands, when we assumed that  $[g_{22}-B]$  is negative for this molecule (see Table II). Our previous fit for BeD<sub>2</sub> was satisfactory<sup>1</sup> and we do not have to switch the  $\Sigma^+(e)$  and  $\Delta(e)$  assignments. However, because the rotational energy is now expressed as a power series in  $[J(J+1)-\ell^2]$ , the rotational constants and the  $g_{22}$  constants are altered (Table III). In this case, if the  $\Sigma^+(e)$  and  $\Delta(e)$  assignments are switched, the standard deviation of the fit increases drastically.

CO<sub>2</sub>, CS<sub>2</sub>, and BeF<sub>2</sub> are good examples of symmetric linear triatomic molecules for which experimental data are available for the  $02^20(\Delta_g)$  and  $02^00(\Sigma_g^+)$  states.<sup>6-8</sup> There is no ambiguity in the assignments for these molecules because

TABLE I. New spectroscopic constants (in  $\text{cm}^{-1}$ ) for  $\text{BeH}_2$ ; all uncertainties are  $1\sigma$ .

BeH <sub>2</sub>	Vibrational levels		
	020 <sup>a</sup>	021	022
Constants			
$G_\Delta$	$a$	$2152.6898(5)+a$	$4272.3113(9)+a$
$g_{22}$	2.6412(29)	2.6107(29)	2.5816(29)
$B_\Delta$	4.721519(23)	4.652203(22)	4.584109(37)
$10^4 D_\Delta$	1.13373(52)	1.11828(50)	1.1012(22)
$10^9 H_\Delta$	3.586(35)	3.549(32)	3.33(42)
$B_\Sigma$	4.723694(38)	4.654358(37)	4.586316(57)
$10^4 D_\Sigma$	1.13964(93)	1.12318(86)	1.1104(34)
$10^9 H_\Sigma$	3.701(64)	3.563(56)	3.99(67)
$10^2 q$	-9.1924(31)	-9.1482(30)	-9.1053(36)
$10^6 q_D$	8.378(62)	8.334(58)	8.31(16)
$10^{10} q_H$	-8.17(38)	-8.46(34)	-10.8(32)

<sup>a</sup>The absolute vibrational energy of the 020 level cannot be determined from our data.

their  $02^00(\Sigma_g^+)$  states are in strong Fermi resonance with the nearby  $10^00(\Sigma_g^+)$  states, and thus lie much lower in energy compared with the  $02^20(\Delta_g)$  states. For metal dihydrides such as  $\text{BeH}_2$ ,  $\text{BeD}_2$ , and  $\text{MgH}_2$ , the sign of  $[g_{22}-B]$  becomes important because the  $B$  values are relatively large. It is interesting to note that the relative locations of the rotational levels of the  $02^00(\Sigma_g^+)$  and  $02^20(\Delta_g)$  states are opposite for  $\text{BeH}_2$  and  $\text{BeD}_2$ . This is simply because the  $g_{22}$  constants of  $\text{BeH}_2$  and  $\text{BeD}_2$  have similar values, but the  $B$  value of  $\text{BeH}_2$  is almost two times larger than that of  $\text{BeD}_2$ . The  $g_{22}$  constant of  $\text{BeD}_2$  is just slightly larger than its  $B$  value, causing the  $\Delta$  state rotational levels to be above those of the  $\Sigma^+$  state. There is also a small vibrational dependence for the  $g_{22}$  constants, as implied by the constants of Tables I–III. Our assignments for the relative positions of the  $\Delta$  and the  $\Sigma^+$  states of  $\text{BeH}_2$  and  $\text{BeD}_2$  are very strongly supported by recent *ab initio* calculations of Li and Le Roy,<sup>9</sup> because the  $g_{22}$  constants predicted by their calculations differ from those of Tables I and III by less than  $0.02 \text{ cm}^{-1}$ .

Small local perturbations (at  $J=18-23$ ) have been observed in the 021 vibrational level ( $\Sigma_u^+$  and  $\Delta_u$ ) of  $\text{BeH}_2$ , which are caused by the nearby 050 vibrational level. The

TABLE II. New spectroscopic constants (in  $\text{cm}^{-1}$ ) for  $\text{MgH}_2$ ; all uncertainties are  $1\sigma$ .

MgH <sub>2</sub>	Vibrational levels	
	020 <sup>a</sup>	021
Constants		
$G_\Delta$	$b$	$1576.5725(8)+b$
$g_{22}$	0.8007(91)	0.7935(91)
$B_\Delta$	2.899710(33)	2.865577(34)
$10^5 D_\Delta$	4.1742(50)	4.1530(57)
$B_\Sigma$	2.900666(58)	2.866519(59)
$10^5 D_\Sigma$	4.2343(88)	4.2094(89)
$10^2 q$	-5.0713(62)	-5.0200(61)
$10^6 q_D$	3.153(66)	3.052(65)

<sup>a</sup>The absolute vibrational energy of the 020 level cannot be determined from our data.

TABLE III. New spectroscopic constants (in  $\text{cm}^{-1}$ ) for  $\text{BeD}_2$ ; all uncertainties are  $1\sigma$ .

BeD <sub>2</sub>	Vibrational levels	
	020 <sup>a</sup>	021
Constants		
$G_\Delta$	$c$	$1671.4484(21)+c$
$g_{22}$	2.5276(85)	2.5134(89)
$B_\Delta$	2.374187(49)	2.343354(54)
$10^5 D_\Delta$	2.757(6)	2.690(7)
$B_\Sigma$	2.374879(89)	2.344138(94)
$10^5 D_\Sigma$	2.804(11)	2.758(12)
$10^2 q$	-2.9795(43)	-2.9858(43)
$10^6 q_D$	1.199(54)	1.157(55)

<sup>a</sup>The absolute vibrational energy of the 020 level cannot be determined from our data.

050 level has three states with  $\Pi_u$ ,  $\Phi_u$ , and  $H_u$  symmetries, and it is not possible to ascertain which state is causing these perturbations using our data. The total energies of the perturbed rotational levels were fitted as individual term values, which are reported in the supplementary tables placed in Electronic Physics Auxiliary Publication Service (EPAPS).<sup>10</sup> The complete lists of the line positions used in our fits have also been placed in the EPAPS archive. We have also refitted all the vibration-rotation bands involving the  $\Pi$  ( $\ell=1$ ) states of  $\text{BeH}_2$ ,  $\text{BeD}_2$ , and  $\text{MgH}_2$  (see the supplementary tables in EPAPS). Due to the  $\ell^2$  terms in the rotational energy expression, the new constants for  $\Pi$  states differ very slightly from those reported in Refs. 1 and 2. Most of the observed vibrational levels of  $\text{BeH}_2$ ,  $\text{BeD}_2$ , and  $\text{MgH}_2$  have  $\Sigma^+$  symmetry and their constants<sup>1,2</sup> remain unchanged because  $\ell$  is equal to zero.

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<sup>10</sup>See EPAPS Document No. E-JCPSA6-124-002615 for complete lists of line positions and constants. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>).