

## **Do Triatomic Molecules Echo Atomic Periodicity?**

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The objective of this work is to test whether vibration frequencies  $\nu_1$  of free, ground-state, main-group triatomic molecules manifest a periodicity similar to those of atomic spectroscopic constants. This test and an earlier test on energies of atomization underscore the role of the periodic law as a foundation of chemistry. Using data from four data bases and from computation, we have collected and have mapped  $\nu_1$  data in mathematical spaces of fixed-period molecules. These spaces are  $9 \times 9 \times 9$ -atom cubes with rare-gas molecules on each face. The  $\nu_1$  collected from various sources might be of use in optical or near-optical searches for cold triatomics in interstellar space.

## 1. Introduction

Diatomic molecules echo atomic periodicity: plotted data for series of molecules in series bounded by diatomics having atomic numbers  $Z_A$  and  $Z_B$  (or both) equal to an atomic magic number are repetitious, and the plots have constant or monotonic amplitude as the molecular masses increase. Gas-phase main-group diatomic molecules AB display this periodic behavior dramatically and allow some reasonably precise predictions to be made.[1,2 ] The properties that have been studied include internuclear separations  $r_e$ ,[3], vibration frequencies  $\omega_e$ ,[3], spring constants  $k_1$ ,[4], ionization potentials[3], and entire Deslandres tables of band-system Frank-Condon factors[5].

Kong [6] found this same periodicity among contracted internuclear distances of free linear/bent *triatomic* molecules (Fig. 1). Babaev has shown periodicity in their structural characteristics [7].

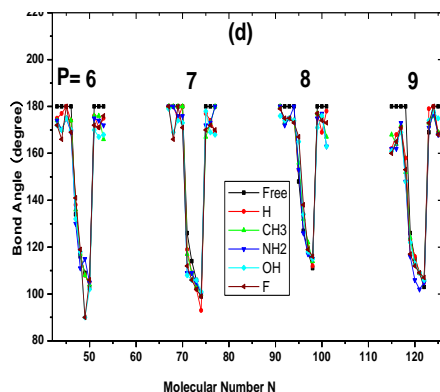


Fig. 1. Percent contracted internuclear distances (dimensionless) [4]. The data are plotted on Kong's molecular number  $N$ , which serves the same role for triatomic molecules in their periodic chart (Fig. 2) as atomic number  $Z$  does for atoms in their periodic chart.  $P$  is the sum of the three atomic period numbers. The black points pertain to free triatomic molecules; the others pertain to "dressed" species, where the atomic number of one outside atom is reduced by 1 and various radicals are attached in its place. When available, the data are from [7]; the remainder are computed at the B3LVP/6/-311G level for  $P = 6$  and 7, and at the B3LVP/LanL2DZ level for  $P = 7$  and 8.

Kong's periodic chart of main-group triatomic molecules (Fig. 2) has the sum of the group numbers (3 to 24) horizontally, and the sum of the period numbers vertically. A molecule whose atoms are in Mendeleev-chart periods 2, 3, 2, or 2,2, 4 has a period sum  $P = 12$ . The first two rows of this chart contain species of no interest in this research. Triatomic molecular numbers are assigned from left to right in  $P = 6$ , then in  $P = 7$ , etc.

P \ G	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	
4	<sup>1</sup> LiH <sub>2</sub> <sup>+</sup>	<sup>2</sup> LiH <sub>2</sub> <sup>+</sup>	<sup>3</sup> LiH <sub>2</sub>	<sup>4</sup> BeH <sub>2</sub>	<sup>5</sup> BH <sub>2</sub>	<sup>6</sup> CH <sub>2</sub>	<sup>7</sup> NH <sub>2</sub>	<sup>8</sup> H <sub>2</sub> O	<sup>9</sup> H <sub>2</sub> F	<sup>10</sup> H <sub>2</sub> Ne	<sup>11</sup> HHeNe	<sup>12</sup> He <sub>2</sub> Ne													
5	<sup>13</sup> LiHe <sub>2</sub>	<sup>14</sup> Li <sub>2</sub> He	<sup>15</sup> Li <sub>2</sub> H	<sup>16</sup> HLiHe	<sup>17</sup> HBe <sub>2</sub>	<sup>18</sup> HBeB	<sup>19</sup> B <sub>2</sub> H	<sup>20</sup> HBC	<sup>21</sup> C <sub>2</sub> H	<sup>22</sup> H <sub>2</sub> CN	<sup>23</sup> N <sub>2</sub> H	<sup>24</sup> HNO	<sup>25</sup> HO <sub>2</sub>	<sup>26</sup> HOF	<sup>27</sup> HF <sub>2</sub>	<sup>28</sup> HFNe	<sup>29</sup> HNNe <sub>2</sub>	<sup>30</sup> HeNe <sub>2</sub>							
6	<sup>31</sup> LiAr <sub>2</sub>	<sup>32</sup> Li <sub>2</sub> Ne	<sup>33</sup> Li <sub>3</sub>	<sup>34</sup> Li <sub>2</sub> Be	<sup>35</sup> LiBe <sub>2</sub>	<sup>36</sup> Be <sub>3</sub>	<sup>37</sup> Be <sub>2</sub> B	<sup>38</sup> BeB <sub>2</sub>	<sup>39</sup> B <sub>3</sub>	<sup>40</sup> B <sub>2</sub> C	<sup>41</sup> C <sub>2</sub> B	<sup>42</sup> C <sub>3</sub>	<sup>43</sup> C <sub>2</sub> N	<sup>44</sup> CN <sub>2</sub>	<sup>45</sup> N <sub>3</sub>	<sup>46</sup> N <sub>2</sub> O	<sup>47</sup> NO <sub>2</sub>	<sup>48</sup> O <sub>3</sub>	<sup>49</sup> FO <sub>2</sub>	<sup>50</sup> F <sub>2</sub> O	<sup>51</sup> F <sub>3</sub>	<sup>52</sup> NeF <sub>2</sub>	<sup>53</sup> Ne <sub>2</sub> F	<sup>54</sup> Ne <sub>3</sub>	
7	<sup>55</sup> NaNe <sub>2</sub>	<sup>56</sup> Li <sub>2</sub> Ar	<sup>57</sup> Li <sub>2</sub> Na	<sup>58</sup> Li <sub>2</sub> Mg	<sup>59</sup> NaBe <sub>2</sub>	<sup>60</sup> Be <sub>2</sub> Mg	<sup>61</sup> NaBe <sub>2</sub>	<sup>62</sup> Be <sub>2</sub> Mg	<sup>63</sup> Be <sub>2</sub> Al	<sup>64</sup> B <sub>2</sub> Si	<sup>65</sup> AlC <sub>2</sub>	<sup>66</sup> SiC <sub>2</sub>	<sup>67</sup> C <sub>2</sub> P	<sup>68</sup> SiN <sub>2</sub>	<sup>69</sup> N <sub>2</sub> P	<sup>70</sup> N <sub>2</sub> S	<sup>71</sup> PO <sub>2</sub>	<sup>72</sup> SO <sub>2</sub>	<sup>73</sup> ClO <sub>2</sub>	<sup>74</sup> SF <sub>2</sub>	<sup>75</sup> ClF <sub>2</sub>	<sup>76</sup> ArF <sub>2</sub>	<sup>77</sup> Ne <sub>2</sub> Cl	<sup>78</sup> Ne <sub>2</sub> Ar	
8	<sup>79</sup> LiAr <sub>2</sub>	<sup>80</sup> Na <sub>2</sub> Ne	<sup>81</sup> Na <sub>2</sub> Li	<sup>82</sup> Na <sub>2</sub> Be	<sup>83</sup> LiMg <sub>2</sub>	<sup>84</sup> Mg <sub>2</sub> Be	<sup>85</sup> Mg <sub>2</sub> B	<sup>86</sup> BeAl <sub>2</sub>	<sup>87</sup> Al <sub>2</sub> B	<sup>88</sup> Al <sub>2</sub> C	<sup>89</sup> Si <sub>2</sub> B	<sup>90</sup> Si <sub>2</sub> C	<sup>91</sup> Si <sub>2</sub> N	<sup>92</sup> CP <sub>2</sub>	<sup>93</sup> P <sub>2</sub> N	<sup>94</sup> P <sub>2</sub> O	<sup>95</sup> NS <sub>2</sub>	<sup>96</sup> S <sub>2</sub> O	<sup>97</sup> S <sub>2</sub> F	<sup>98</sup> Cl <sub>2</sub> O	<sup>99</sup> Cl <sub>2</sub> F	<sup>100</sup> NeCl <sub>2</sub>	<sup>101</sup> Ar <sub>2</sub> F	<sup>102</sup> Ar <sub>2</sub> Ne	
9	<sup>103</sup> NaAr <sub>2</sub>	<sup>104</sup> Na <sub>2</sub> Ar	<sup>105</sup> Na <sub>3</sub>	<sup>106</sup> Na <sub>2</sub> Mg	<sup>107</sup> NaMg <sub>2</sub>	<sup>108</sup> Mg <sub>3</sub>	<sup>109</sup> Mg <sub>2</sub> Al	<sup>110</sup> MgAl <sub>2</sub>	<sup>111</sup> Al <sub>3</sub>	<sup>112</sup> Al <sub>2</sub> Si	<sup>113</sup> AlSi <sub>2</sub>	<sup>114</sup> Si <sub>3</sub>	<sup>115</sup> Si <sub>2</sub> P	<sup>116</sup> SiP <sub>2</sub>	<sup>117</sup> P <sub>3</sub>	<sup>118</sup> P <sub>2</sub> S	<sup>119</sup> PS <sub>2</sub>	<sup>120</sup> S <sub>3</sub>	<sup>121</sup> S <sub>2</sub> Cl	<sup>122</sup> S <sub>2</sub> Cl <sub>2</sub>	<sup>123</sup> Cl <sub>3</sub>	<sup>124</sup> ArCl <sub>2</sub>	<sup>125</sup> Ar <sub>2</sub> Cl	<sup>126</sup> Ar <sub>3</sub>	
10	<sup>127</sup> KAr <sub>2</sub>	<sup>128</sup> Na <sub>2</sub> Kr	<sup>129</sup> Na <sub>2</sub> K	<sup>130</sup> Na <sub>2</sub> Ca	<sup>131</sup> KMg <sub>2</sub>	<sup>132</sup> Mg <sub>2</sub> Ca	<sup>133</sup> Mg <sub>2</sub> Ga	<sup>134</sup> CaAl <sub>2</sub>	<sup>135</sup> Al <sub>2</sub> Ga	<sup>136</sup> Al <sub>2</sub> Ge	<sup>137</sup> GaSi <sub>2</sub>	<sup>138</sup> Si <sub>2</sub> Ge	<sup>139</sup> Si <sub>2</sub> As	<sup>140</sup> GeP <sub>2</sub>	<sup>141</sup> P <sub>2</sub> As	<sup>142</sup> P <sub>2</sub> Se	<sup>143</sup> As <sub>2</sub> S <sub>2</sub>	<sup>144</sup> SeS <sub>2</sub>	<sup>145</sup> S <sub>2</sub> Br <sub>2</sub>	<sup>146</sup> Se <sub>2</sub> Cl	<sup>147</sup> BrCl <sub>2</sub>	<sup>148</sup> KrCl <sub>2</sub>	<sup>149</sup> Ar <sub>2</sub> Br	<sup>150</sup> Ar <sub>2</sub> Kr	
11	<sup>151</sup> NaKr <sub>2</sub>	<sup>152</sup> K <sub>2</sub> Ar	<sup>153</sup> NaK <sub>2</sub>	<sup>154</sup> K <sub>2</sub> Mg	<sup>155</sup> NaCa <sub>2</sub>	<sup>156</sup> MgCa <sub>2</sub>	<sup>157</sup> Ca <sub>2</sub> Al	<sup>158</sup> MgGa <sub>2</sub>	<sup>159</sup> AlGa <sub>2</sub>	<sup>160</sup> Ga <sub>2</sub> Si	<sup>161</sup> AlGe <sub>2</sub>	<sup>162</sup> SiGe <sub>2</sub>	<sup>163</sup> Ge <sub>2</sub> P	<sup>164</sup> SiAs <sub>2</sub>	<sup>165</sup> PAs <sub>2</sub>	<sup>166</sup> As <sub>2</sub> S	<sup>167</sup> Se <sub>2</sub> P	<sup>168</sup> Se <sub>2</sub> S	<sup>169</sup> SeCl <sub>2</sub>	<sup>170</sup> S <sub>2</sub> Br <sub>2</sub>	<sup>171</sup> Br <sub>2</sub> Cl	<sup>172</sup> ArBr <sub>2</sub>	<sup>173</sup> Kr <sub>2</sub> Cl	<sup>174</sup> ArKr <sub>2</sub>	
12	<sup>175</sup> KKr <sub>2</sub>	<sup>176</sup> K <sub>2</sub> Ar	<sup>177</sup> K <sub>3</sub>	<sup>178</sup> K <sub>2</sub> Ca	<sup>179</sup> Ca <sub>2</sub> K	<sup>180</sup> Ca <sub>3</sub>	<sup>181</sup> Ca <sub>2</sub> Ga	<sup>182</sup> CaGa <sub>2</sub>	<sup>183</sup> Ga <sub>3</sub>	<sup>184</sup> Ga <sub>2</sub> Ge	<sup>185</sup> GaGe <sub>2</sub>	<sup>186</sup> Ge <sub>3</sub>	<sup>187</sup> Ge <sub>2</sub> As	<sup>188</sup> GeAs <sub>2</sub>	<sup>189</sup> As <sub>3</sub>	<sup>190</sup> As <sub>2</sub> Se	<sup>191</sup> AsSe <sub>2</sub>	<sup>192</sup> Se <sub>3</sub>	<sup>193</sup> Se <sub>2</sub> Br	<sup>194</sup> SeBr <sub>2</sub>	<sup>195</sup> Br <sub>3</sub>	<sup>196</sup> KrBr <sub>2</sub>	<sup>197</sup> Kr <sub>2</sub> Br	<sup>198</sup> Kr <sub>3</sub>	
13	<sup>199</sup> RbKr <sub>2</sub>	<sup>200</sup> K <sub>2</sub> Xe	<sup>201</sup> K <sub>2</sub> Rb	<sup>202</sup> K <sub>2</sub> Sr	<sup>203</sup> RbCa <sub>2</sub>	<sup>204</sup> Ca <sub>2</sub> Sr	<sup>205</sup> Ca <sub>2</sub> In	<sup>206</sup> SrGa <sub>2</sub>	<sup>207</sup> Ga <sub>2</sub> In	<sup>208</sup> Ga <sub>2</sub> Sn	<sup>209</sup> InGe <sub>2</sub>	<sup>210</sup> Se <sub>2</sub> Sn	<sup>211</sup> Ge <sub>2</sub> Sb	<sup>212</sup> SnAs <sub>2</sub>	<sup>213</sup> As <sub>2</sub> Sb	<sup>214</sup> As <sub>2</sub> Te	<sup>215</sup> SbSe <sub>2</sub>	<sup>216</sup> Se <sub>2</sub> Te	<sup>217</sup> Se <sub>2</sub> I	<sup>218</sup> TeBr <sub>2</sub>	<sup>219</sup> Br <sub>2</sub> Cl	<sup>220</sup> XeBr <sub>2</sub>	<sup>221</sup> Kr <sub>2</sub> I	<sup>222</sup> Kr <sub>2</sub> Xe	
14	<sup>223</sup> KXe <sub>2</sub>	<sup>224</sup> Rb <sub>2</sub> Kr	<sup>225</sup> KRb <sub>2</sub>	<sup>226</sup> Rb <sub>2</sub> Ca	<sup>227</sup> KSr <sub>2</sub>	<sup>228</sup> CaSr <sub>2</sub>	<sup>229</sup> Sr <sub>2</sub> Ga	<sup>240</sup> CaIn <sub>2</sub>	<sup>241</sup> GaIn <sub>2</sub>	<sup>242</sup> In <sub>2</sub> Ge	<sup>243</sup> GaSn <sub>2</sub>	<sup>244</sup> SeSn <sub>2</sub>	<sup>245</sup> SnAs <sub>2</sub>	<sup>246</sup> GeSb <sub>2</sub>	<sup>247</sup> AsSb <sub>2</sub>	<sup>248</sup> Sb <sub>2</sub> Se	<sup>249</sup> AsTe <sub>2</sub>	<sup>250</sup> SeTe <sub>2</sub>	<sup>251</sup> Te <sub>2</sub> Br	<sup>252</sup> SeI <sub>2</sub>	<sup>253</sup> BrI <sub>2</sub>	<sup>254</sup> KrI <sub>2</sub>	<sup>255</sup> Xe <sub>2</sub> Br	<sup>256</sup> KrXe <sub>2</sub>	
15	<sup>257</sup> RbXe <sub>2</sub>	<sup>258</sup> Rb <sub>2</sub> Xe	<sup>259</sup> Rb <sub>3</sub>	<sup>260</sup> Rb <sub>2</sub> Sr	<sup>261</sup> RbSr <sub>2</sub>	<sup>262</sup> Sr <sub>3</sub>	<sup>263</sup> Sr <sub>2</sub> In	<sup>264</sup> SrIn <sub>2</sub>	<sup>265</sup> In <sub>3</sub>	<sup>266</sup> SnIn <sub>2</sub>	<sup>267</sup> Sn <sub>2</sub> In	<sup>268</sup> Sn <sub>3</sub>	<sup>269</sup> SnSb <sub>2</sub>	<sup>270</sup> Sn <sub>2</sub> Sb	<sup>271</sup> Sb <sub>3</sub>	<sup>272</sup> Sb <sub>2</sub> Te	<sup>273</sup> SbTe <sub>2</sub>	<sup>274</sup> Te <sub>3</sub>	<sup>275</sup> Te <sub>2</sub> I	<sup>276</sup> TeI <sub>2</sub>	<sup>277</sup> I <sub>3</sub>	<sup>278</sup> XeI <sub>2</sub>	<sup>279</sup> Xe <sub>2</sub> I	<sup>280</sup> Xe <sub>3</sub>	

Fig. 2. Kong’s periodic system of main-group triatomic molecules [9]. The table has the sums of the atomic group and period numbers  $G$  from left to right and  $P$  down from top to bottom. After  $P = 4$  and 5, which are devoted to hydrides, the cells show the simplest triatomic molecules; other isoelectronic species can be found by proton shifting.

These and other results for diatomic and triatomic molecules underscore the role of the *periodic law* as a foundation of chemistry, and thus support the argument that chemistry is not a special case of physics (the subject of prolonged debate [*e.g.* 10]).

The objectives of this work are to test for periodicity in heats of atomization of free triatomic molecules, and in addition to prepare for testing triatomic molecular longitudinal symmetric-stretch vibration frequencies  $\nu_1$ . The test for this property will entail additional work; even the beginning of this work – entailing only  $P = 6$  molecules – occupies much of this paper. The spectroscopic constant  $\nu_1$  was chosen partly with the hope that it may be distributed in triatomic molecular space as smoothly as diatomic molecular vibration frequencies are in diatomic molecular space [11]. It was also chosen in the hope that the collected data might assist astrophysicists in visible and near-visible light searches for cold triatomic molecules in circumstellar space.

## 2. Theory

### 2.1. Chemical considerations

This investigation does not address the whether any particular free triatomic exists in the observable universe or in experimental apparatus. All of them are considered candidates for existence in some unexplored location in the cosmos or for a brief existence as transition species.

Aside from this, considerations such as bond types, bond orders, cyclic isomers, multiplicities, chemical or radioactive reactivity, and behavior when in the solid or liquid state, are ignored in this study.

### 2.2. Molecular mechanics

The symmetric-stretch vibration frequency of a linear, symmetric, triatomic molecule is given by the standard equation for a mass hanging on a spring:

$$\nu_1 = (1/2\pi)\sqrt{k_1/m} \quad (1)$$

where  $k_1$  is the force constant appropriate for the motion and  $m$  is the mass of either outer atom [12]. The equation for  $\nu_1$  is almost the same as that for the vibration frequency  $\omega_e$  of a diatomic molecule; the only change needed in Eq. (1) is to replace  $m$  by the reduced mass:

$$\omega_e = (1/2\pi)\sqrt{k_1/\mu} \quad (2)$$

It follows that  $\nu_1$  of a linear, symmetric, triatomic molecule ABA can be obtained from  $\omega_e$  of the diatomic molecule AB by

$$\nu_1 = \omega_e\sqrt{\mu/m} \quad (3)$$

This conversion will be used in the section on data acquisition. The equations for non-linear, non-symmetric, or non-linear and non-symmetric triatomics [12] were not used in this work.

### 2.3. The space for linear/bent triatomic molecules

Being able to visualize this mathematical space is essential for understanding what follows in this paper. First, imagine an  $8 \times 8 \times 8$ -atom cube populated by main-group period-2 atoms with rare-gas molecules on three faces. Then generalize to many such cubes, ranging from  $(R_1, R_2, R_3) = (2, 2, 2)$  to  $(7, 7, 7)$  (Fig. 3) where  $R_i$  is the period number of atom  $i$ . The result is the molecular mathematical space for neutral main-group triatomic molecules.

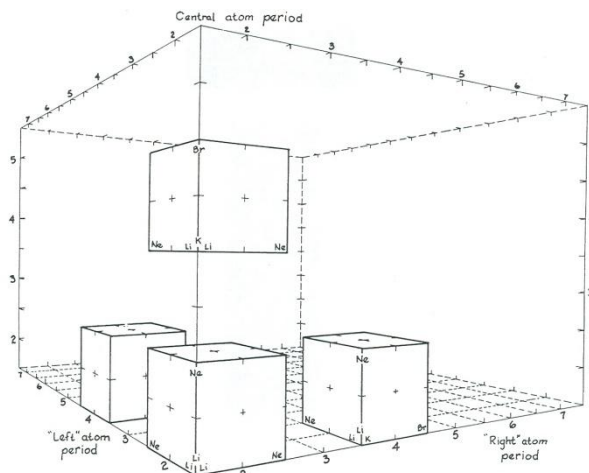


Fig. 3. The space for main-group triatomic molecules formed from atoms  $(R_1, R_2, R_3) = (2, 2, 2)$  to  $(7, 5, 7)$ ; hydrogen and helium ( $R_i = 1$ ) are omitted. The diagram is symmetric with respect to reflection in a plane containing the closest and the farthest edges of the space; hence the cube with periods  $(R_1, R_2, R_3) = (4, 2, 2)$  contains the same molecules as does the cube  $(2, 2, 4)$ . It follows that one of these cubes is redundant. There are  $\{[(6 \times 5)/2] \times 7\} = 105$  non-redundant cubes, each containing  $8 \times 8 \times 8 = 512$  molecules, making a total of 53,760 molecules. There are 49 cubes with  $R_1 = R_2$ , each containing  $\{[(8 \times 9)/2] \times 8\} = 288$  molecules, making a total of 14,112 molecules. Thus, the total population of all the space is 67,872.

The features inside the individual cubes (subspaces) are important. Fig. 4 shows horizontal cuts made for various central atoms; they are enumerated by the group number,  $C_2$ , of the central atom. If the cube is selected from  $R_1 = R_2$ , then the molecules on each cut are symmetric to reflection through the line  $C_1 = C_3$ ; otherwise species on opposite sides of the line  $C_1 = C_3$  are not redundant.

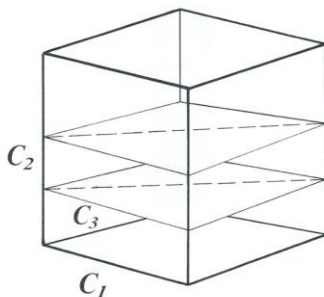


Fig. 4. Sample horizontal cuts for different central atoms,  $C_2$ , of any cube in Fig. 3. The figure is rotated approximately  $90^\circ$  with respect to those in Fig. 3 and is not to scale.

The cubes may be sliced by other planes, for example planes containing isoelectronic molecules (Fig. 5). The slicing may be done while the cubes are all packed into the space of Fig. 1, with the result that an isoelectronic sequence will have members in more than one cube.

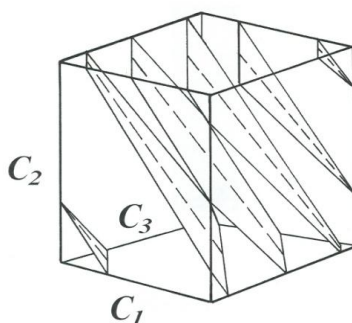


Fig. 5. Sample isoelectronic slices in any subspace of Fig. 3. As the total electron count  $n_e$  increases, the slices progress from a triangle at the lower left, to a truncated triangle, to a hexagon, and back with reverse orientation toward the upper right. The dashed lines in the figure pass through the locations of symmetric molecules that lie on the vertical plane  $C_1 = C_3$  of Fig. 3.

### 3. Data acquisition

#### 3.1. Tabulated triatomic vibration frequencies

The National Institute of Science and Technology Webbook [8] provides data for many known triatomics. Webbook data were used except those ABC species where  $\nu_1$  and  $\nu_3$  were identified as the “AB stretch” and “BC stretch.” The most recent  $\nu_1$  datum was always used, without regard to the method used to obtain it. An earlier compilation by Krasnov [13] was also consulted to obtain vibration frequencies. Its values were used where the Webbook was silent.

#### 3.2. Linear symmetric molecules as a special case

The Handbook for Physics and Chemistry [14] and “Constants of Diatomic Molecules” by Huber and Herzberg [15], provide  $\omega_e$  for two-atom (AB) molecules. Using Eq. (3) and a table of atomic masses make it possible to calculate  $\nu_1$  for the triatomics ABA. This calculation is very useful because data for several triatomic molecules can be obtained that are not accessible in [11] or [12]. Table 1 presents data obtained in this way.

Table 1. Linear symmetric triatomic symmetric-stretch vibration frequencies obtained using Eq. (3). All values have been rounded to one significant figure after the decimal point.

$(R_1, R_2, R_3)$	$n_e$	Molecule		$\nu_1$	Reference
		Diatomic	Triatomic		
(2,2,2)	13	LiN	LiNLi	379.5	[15]
	14	LiO	LiOLi	470.1	[15]
	15	LiF	LiFLi	472.8	[15]
	15	B <sub>2</sub>	B <sub>3</sub>	750.2	[15]
	22	BeF	FBeF	707.5	[15]
	22	NO	ONO	1301.0	[15]
	22	NO	NON	1390.3	[15]
	24	BF	FBF	849.3	[15]

<sup>a</sup> The datum “corresponds to  $\Delta G(1/2)$  or the lowest observed integral”

### 3.3. Computations for Molecules

We employed two *ab initio* chemistry modeling programs on the Georgia Institute of Technology WebMo graphical user interface: QChem and PSI4. Within the graphical user interface, a molecule was built each time with single bonds connecting the atoms. The molecule then had its mechanics “optimized” for bond lengths and bond angle. The Hartree-Fock method, the “optimization and vibration Frequency” option, the “unrestricted” reference, and the automatically recommended multiplicity were always used; then the computer determined the optimum bond lengths and angles for the molecule.

This protocol was used for each of the several basis sets. For the (2,2,2) space, we primarily used 6-31+G(d) and 6-311+G(d,p) (identical to 6-31+G\* and 6-311+G\*\* respectively) basis sets using the QChem software. We also used aug-cc-pVDZ and pVQZ basis sets with PSI4 software. These latter choices took substantially more computational time than any QChem bases: while either basis in QChem would take between 1 and 20 minutes, and aug-cc-pVDZ within PSI4 would take just under an hour’s time, aug-cc-pVQZ could run for as many as 30 hours per molecule.

While queuing jobs for the Georgia Tech computer to process throughout the day and overnight, we would request it to run using three bases for each molecule: usually 6-311+G\*\*, aug-cc-pVDZ, and aug-cc-pVQZ. By doing so, we hoped to obtain at least one successful result by having more than one basis; to save time; and to establish whether or not the computer agreed with itself for a given molecule.

Van der Waal's bonds are considered to pertain to cases where the computed molecular results indicated dissociation.

The symbols  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  are almost always used to represent the symmetric-stretch, bending, and asymmetric-stretch vibration modes. Occasionally the values found were such that  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  are in actuality  $\nu_3$ ,  $\nu_2$ , and  $\nu_1$ ; for these,  $\nu_1$  and  $\nu_3$  were reversed.

## 4. Analysis of data

### 4.1. Specifics of the molecular space

As data for a given  $(R_1, R_2, R_3)$  were acquired, they were placed in bins of constant total electron count  $n_e$ . It is here that Fig. 5 must be consulted – in particular, the dashed lines within the various planes of fixed  $n_e$ . Falling along these dashed lines are symmetric molecules enumerated by  $C_2$ . Now consider the subspace containing molecules with atoms from  $(R_1, R_2, R_3) = (2, 2, 2)$ . Species containing rare-gas atoms were ignored, so the least and greatest total electron counts pertain to  $\text{Li}_3$  and  $\text{F}_3$ :

$$C_1 + C_2 + C_3 = k, \quad 3 \leq k \leq 21 \quad . \quad (4)$$

where  $C_i$  is the integer group number of atom  $i$  in short form periodic charts,  $1 \leq C_i \leq 7$ . Within each bin, the data were entered in order of  $C_2$ . If the molecules are symmetric,  $C_1 = C_3$ , and

$$C_1 = (k - C_2)/2 \quad . \quad (5)$$

Table 2 shows solutions of this equation for integer values of  $C_2$  and  $C_1$  that yield symmetric molecules bounded, in  $C_2$  for a given  $k$ , by species with rare-gas atoms. Several aspects deserve attention:

- The bins do not have the same numbers of occupants
- The generalization to non-symmetric molecules is trivial: decrease  $C_1$  by 1 and increase  $C_3$  by 1. This process generate new molecules which could be horizontal in Table 1 and which would eventually end with rare-gas molecules.
- The generalization to molecules with atoms from other periods is trivial



Table 2. Solutions of Eq. (5) for  $(R_1, R_2, R_3) = (2, 2, 2)$  molecules. Values of  $C_1$ ,  $C_2$ , or  $n_e$  that are half-integer or negative, and molecules with one or more rare-gas atom, have been deleted.

$K$	$C_2$	$C_1$	$n_e$	Molecule	$k$	$C_2$	$C_1$	$n_e$	Molecule
4	2	1	10	LiBeLi	18	12	2	5	BBeB
5	1	2	11	BeLiBe		12	4	4	CCC
5	3	1		LiBLi		12	6	3	BOB
6	2	2	12	BeBeBe	19	13	1	6	OLiO
6	4	1		LiCLi		13	3	5	NBN
7	1	3	13	BLiB		13	5	4	CNC
7	3	2		BeBBe		13	7	3	BFB
7	5	1		LiNLi	20	14	2	6	OBeO
8	2	3	14	BBeB		14	4	5	NCN
8	4	2		BeCBe		14	6	4	COC
8	6	1		LiOLi	21	15	1	7	FLiF
9	1	4		CLiC		15	3	6	OBO
9	3	3	15	BBB		15	5	5	NNN
9	5	2		BeNBe		15	7	4	CFC
9	7	1		LiFLi	22	16	2	7	FBeB
10	2	4	16	CBeC		16	4	6	OCO
10	4	3		BCB		16	6	5	NON
10	6	2		BeOBe	23	17	3	7	FBF
11	1	5	17	NLiN		17	5	6	ONO
11	3	4		CBC		17	7	5	NFN
11	5	3		BNB	24	18	4	7	FCF
11	7	2		BeFBe		18	6	6	OOO
Continued at right					25	19	5	7	FNF
					26	20	6	7	FOF

## 4.2. Tabulating the results

As the molecular vibration frequencies were being placed into a master file, they were plotted on  $C_2$  (Fig. 6) as a running check on the data-entry process. In the cases where two or more tabulated or computational results for a given molecules did not fall as close or closer together than shown in the figure, then the outliers were dropped.

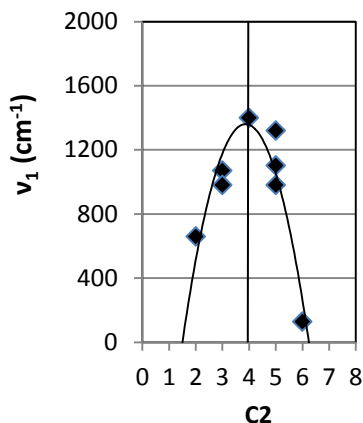


Fig. 6. A graphic produced as a cross-check while data were being introduced into the portion of the main file for molecules with  $n_e = 21$ . Vibration frequencies  $\nu_1$  are plotted on  $C_2$ .  $C_2 = 0$  and 8 relate to rare-gas molecules. The parabolic fit has only a suggestive role; a more realistic curve might intersect the abscissa at 1 and 7. The very low-value datum at  $C_2 = 6$  would normally have been ignored but in this case was retained. The figure gives a sense of the spreads of data for which averages and error measures were calculated. Additional discussion of these measures follows in Section 4.3.

The resulting data are presented in Table 3. The molecules shown are far from being the totality of all molecules that would fill their space for several reasons:

- Large numbers of molecules are not in the tables and requests for computational values were rejected
- Any molecular computation which resulted in imaginary or negative values of  $\nu_1$ , or presented the molecule as being cyclic, were discarded
- Any result for  $\nu_1$  and  $\nu_3$  designated as AB and BC stretches was discarded
- Results including single- or double-digit vibration frequencies were dropped except if the molecules'  $C_2$  values were close to the limiting values (Section 4.2)
- If data from **K**, **H**, or **P** differed seriously from **W** or from the surrounding  $\nu_1$ , they were ignored

Table 3. Data for molecules from (R1,R2,R3) = (2,2,2) in order of  $n_e$  and then  $C_2$ . The averages are derived from computed values (**A**: aug-cc-pVDZ; **C**: aug-cc-pVQZ; **D**, 6-311+G\*\*;; **L**, 6-31G(d); and **M**, 6-311+G(d,p) when successful – and tabulated values (**W**, [8]; **K**, [13]; **P**, [14]; **H**, [15] with Eq. (3) – where available). “**2M;KW**” means the **M** was successful two times and slightly different tabulated values were found in **K** and **W**. If two sources contributed, then the half-difference error is shown in column 4; if more contributed then the sample standard deviation is shown. All values are rounded to one significant figure after the decimal. End-notes to the table state the causes of percent errors in excess of 10%.

$n_e$	Species	Average $\nu_1$ (cm <sup>-1</sup> )	Difference error, or $\sigma$	Percent error or $\sigma$	Table or basis
11	LiBeBe	388.4			<b>C</b>
12	BeBeBe	539.5	1.5	0.3	<b>AD</b>
	LiBeB	356.6	40.0	11.2 <sup>a</sup>	<b>AD</b>
	LiBBe	533.2	0.2	0.0	<b>2C</b>
	LiCLi	570.9			<b>A</b>
13	BBeBe	443.8			<b>M</b>
	LiCBe	626.3			<b>M</b>
	LiNLi	772.8			<b>A</b>
14	BBeB	762.2			<b>A</b>
	BeBB	635.4			<b>A</b>
	LiOLi	817.2	33.2	3.8	<b>A,C;W</b>
15	BBeC	534.6			<b>A</b>
	BBB	535.3			<b>H</b>
	BeCB	1218.6	0.3	0.0	<b>C,D</b>
	BeNBe	1290.3	2.0	0.2	<b>2D</b>
	BNLi	764.1	2.8	0.4	<b>AD</b>
	BeOLi	840.1			<b>C</b>
	LiFLi	672.2			<b>H</b>
16	BeBeO	693.2			<b>W</b>
	CBeC	1130.0	1.3	0.1	<b>CD</b>
	LiNC	2080.4			<b>K</b>
	BeOBe	1083.4	38.4	3.5	<b>2M;KW</b>
17	BBeO	475.4 <sup>b</sup>			<b>L</b>
	CBeN	760.8			<b>A</b>
	BeBeF	458.4	179.4	39.1 <sup>a</sup>	<b>CD</b>
	BeBO	646.9	31.7	4.9	<b>D,M</b>
	LiBF	243.3	21.9	9.0	<b>AC3G</b>
	CCB	1526.1			<b>M</b>

	BNB	1290.8			<b>L</b>
	LiCO	652.2			<b>M</b>
	BeOB	493.3			<b>M</b>
18	NBeN	520.0			<b>A</b>
	BBO	617.5	48.7	7.9	<b>C,M</b>
	CCC	1224.5			<b>W</b>
	BCN	863.7	177.0	20.5 <sup>c</sup>	<b>ACDM</b>
	BOB	1113.0			<b>M</b>
	BeFB	19.4			<b>M</b>
	LiFC	605.0			<b>M</b>
19	OLiO	719.7			<b>W</b>
	CNC	1123.0	77.0	6.9	<b>MK</b>
	BNN	957.4	0.7	0.1	<b>M;K</b>
	BeNO	759.6	154.2	20.3 <sup>d</sup>	<b>M,W</b>
	LiOF	804.1			<b>M</b>
	BeON	1439.5			<b>M</b>
	BOC	1141.5			<b>M</b>
20	OBeO	1060.5			<b>M</b>
	NCN	1338.0	122.1	9.1	<b>2A;W</b>
	CCO	1970.9			<b>W</b>
	COC	1096.1			<b>M</b>
21	OBeF	660.1			<b>A</b>
	OBO	1070.0			<b>W</b>
	NBF	980.4			<b>A</b>
	NCO	1398.7			<b>A</b>
	BNF	980.3			<b>M</b>
	CNO	1103.2			<b>A</b>
	NNN	1320.0			<b>W</b>
	BeOF	128.6	5.5	4.3	<b>2A</b>
22	FBeF	735.6	31.1 <sup>c</sup>	2.6	<b>A;H,W</b>
	OBF	1076.1	37.0	3.4	<b>A,C,D;W</b>
	OCO	1425.7	92.7	6.5	<b>D;W</b>
	NCF	1205.0			<b>C</b>
	BOF	1059.8			<b>A</b>
	NON	1076.8			<b>A</b>
23	FBF	1153.0			<b>W</b>
	OCF	1861.6			<b>W</b>
	ONO	1318.0			<b>W</b>
	FCF	1225.1			<b>W</b>
24	FNO	945.4	0.6	0.1	<b>D,M</b>
	NOF	1103.0			<b>W</b>
	OOO	1103.0			<b>W</b>
	FNF	1075.0			<b>W</b>

25	OOF	1491.0	4.0	0.3	<b>K,W</b>
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- <sup>a</sup> The computation from 6-311+G\*\* is considerably higher in this instance than that for aug-c-pVDZ
- <sup>b</sup> This 6-31G(d) value is next to a rare gas vibration frequency, presumed to be very small. If the 6-311+G(d,p) result of 1053.8 is retained, then columns 2 to 4 contain 746.6, 289.2, and 37.8,
- <sup>c</sup> The computation from 6-311+G\*\* is again considerably higher than those for aug-c-pVDZ and pVQZ, and 6-311+G(d,p)
- <sup>d</sup> The result from 6-311+G(d,p) is low with respect to the Webbook value.
- <sup>e</sup> The Huber and Herzberg value used in Eq. (4) is doubtful because it may refer to  $\omega_e$  for a vibrational level higher than  $v'' = 0$

### 4.3. The distribution of molecules in their space

For every molecule ABC the data in the file were reversed so as to include the molecule CBA. All of these were then plotted in the  $(C_1, C_2, C_3)$  coordinates of the appropriate subspace of Fig. 3. Fig. 7 shows  $\nu_1$  having the highest values, from 2230 down to 1200  $\text{cm}^{-1}$ . It can be seen that they all have carbon, nitrogen, and oxygen as their central atoms. Fig. 8 presents all of the  $\nu_1$  values gleaned in this study.

As explained in Section 4.2, the failure of Fig. 8 to show a completely filled molecular subspace is due to the absence of so many molecules in [13 and 14] and to the failure of many of the computations.

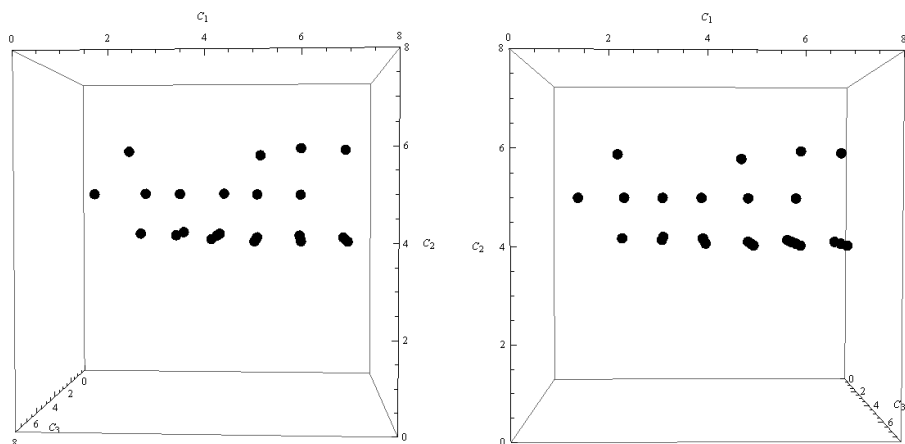


Fig. 7. Stereoscopic view of vibration frequencies for molecules in the subspace  $(R_1, R_2, R_3) = (2, 2, 2)$  having the high-end  $\nu_1$  values from 2230 down to 1200  $\text{cm}^{-1}$ . The data are symmetric with respect to reflection through the  $C_1 = C_3$  plane, which passes through the near vertical edge at right and the far vertical edge at left.

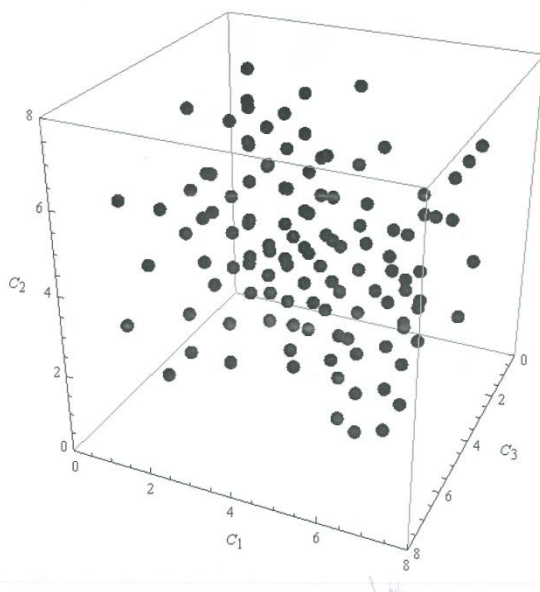


Fig. 8. Vibration frequencies for all molecules in the subspace  $(R_1, R_2, R_3) = (2, 2, 2)$ . This subspace is the cube in Fig. (3) which lies closest to the reader.

#### 4.4. analysis of errors

After the entries were vetted as discussed above Fig. 6, and before the introduction of reversed values (Section 4.2), the data for each molecule having more than one entry were averaged.

Percent errors of these means were estimated as follows: if there were two data (29% of the instances),

$$\text{Percent error} = (v_{1,1} - v_{1,2}) * 100/X \quad , \quad (6)$$

where X is the Webbook value if there is one, and otherwise is the mean of all tabulated and computed results for the molecule. If there were more than two data (12% of the instances) the percent errors were replaced by sample standard deviations.

The percent errors of means of computed vibration frequencies are shown in Table 4.

Table 4. Means, combined random and systematic errors (rows 1 to 5, where X is NIST Webbook), and random errors (rows 6 to 10, where X represents the for results from computations or compilations. Basis sets not shown had one result or no obtained result. All values rounded to one significant figure after the decimal point.

Table or basis set	X	Entries	Mean $\nu_1$ in $\text{cm}^{-1}$	Percent error of mean
aug-cc-pVDZ	[8]	2	9.3	9.6
aug-cc-pVQZ	[8]	8	-5.5	18.4
6-311+G**	[8]	5	-12.2	27.5
6-311+G(d,p)	[8]	4a	5.9	3.7
[13]	[8]	3	-1.1	3.2
aug-cc-pVDZ	Our mean	25	-1.5	7.0
aug-cc-pVQZ	Our mean	21	-2.8	12.4
6-311+G**	Our mean	28	0.9	5.3
6-311+G(d,p)	Our mean	7a	1.6	4.4
[14]	Our mean	3	0.0	2.6

<sup>a</sup> One two digit value of  $\nu_1$  was omitted from the statistics. This value was adjacent to a rare-gas molecule and contributed to the correct decline of the parabola (Fig. 6) toward zero.

In one case (row 9) the standard deviation is smaller than the average. In the other cases, the averages are *statistically* not different from zero.

## 5. Demonstration of periodicity

Triatomic molecular heats of atomization provide an excellent manifestation of periodicity. It is difficult if not impossible to visualize trends in the six-dimensional space within which the data

for triatomic molecules lie, so a collapsed coordinate system is used. The coordinates of this system are  $n_e$ ,  $C_2$ , and (from frame to frame below)  $f(R)$  is

$$f(R) = R_1R_2 + R_2R_3 \quad . \quad (7)$$

This formula for  $f(R)$  was found earlier [16] by plotting data for fixed-group molecules on various functions of the atomic period numbers, such as  $R_1 + R_2 + R_3$  and  $R_1R_2R_3$ . From among these, the plots showed  $f(R)$  to be the superior independent variable.

It is remarkable that data for spectroscopic constants of fixed-period [fixed  $f(R)$ ] molecules are often found to have similar values in series with fixed

$$G(C) = C_1+2C_2+C_3 = (C_1+C_2) + (C_2+C_3), \quad (8)$$

as often or more so than in isoelectronic series with fixed  $C_1+C_2+C_3$ . Eqs. (7) and (8) define a simple Diatomics-in-Molecules method for data plotting.

Energies of atomization for molecules with fixed period numbers  $f(R) = R_1R_2 + R_2R_3$ , plotted on coordinates enumerated by  $n_e$  and  $C_2$  are shown in the following figures, which clearly show periodicity of triatomic  $\Delta_a H$ .

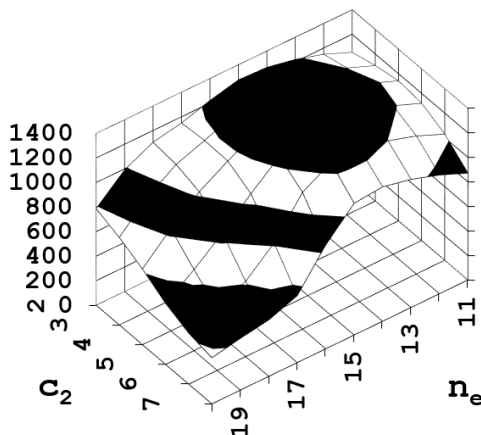


Fig. 9.  $\Delta_a H$  in kJ/mol for  $f(R) = 8$ , i.e.,  $(R_1, R_2, R_3) = (2, 2, 2)$ . This plot and those that follow are the result of a neural-network model built from available data.



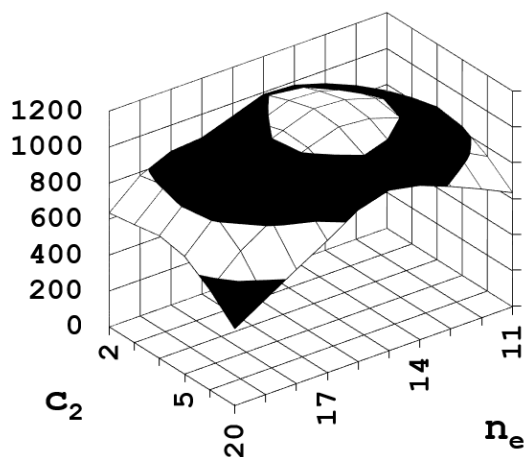


Fig. 10.  $\Delta_a H$  in kJ/mol for  $f(R) = 16$ , i.e.,  $(R_1, R_2, R_3) = (2, 4, 2)$ ,  $(4, 2, 4)$ ,  $(6, 2, 2)$ , and  $(2, 2, 6)$ . Permuted period numbers do not result in redundancies, but for each  $f(R)$  any intersection of the fishnet surface may represent several molecules. Hence, given both  $f(R)$  it follows that each intersection may be populated by very many molecules. The ordinates of the graph are neural-network “averages” based on all known data, so it is clear that any attempt to predict  $\Delta_a H$  at any location would be futile.

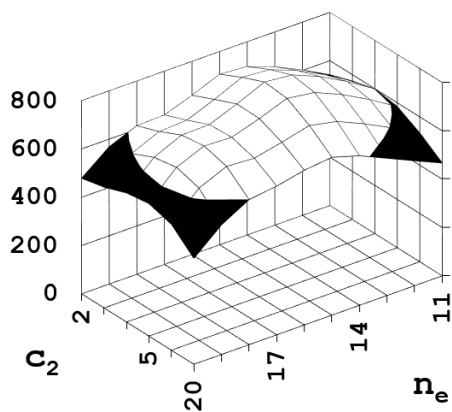


Fig. 11. Same as Fig. 10 except for  $f(R) = 28$ , i.e.,  $(R_1, R_2, R_3) = (5, 2, 4)$ ,  $(4, 2, 5)$ ,  $(5, 6, 2)$ ,  $(6, 2, 5)$ ,  $(2, 7, 2)$ , and  $(7, 2, 7)$ . A second hump at  $n_e = 17$  is visible.

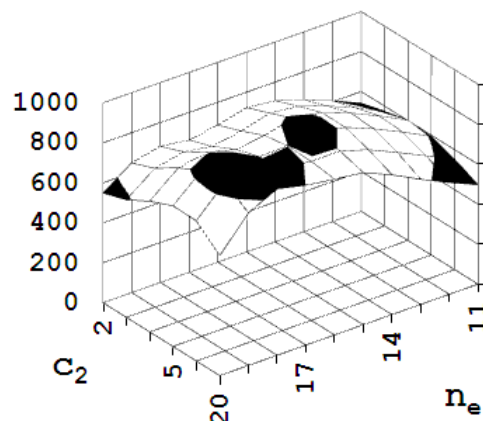


Fig. 12. Same as Fig. 10 except for  $f(R) = (5,6,5)$  or  $(6,5,6) = 60$ . The amplitudes of the figures decrease monotonically as  $f(R)$  increases, a requisite for claiming periodic behavior. The second hump visible in Fig. 11 has grown relatively larger while still within the monotonic constraint. .

## 6. Discussion

Periodicity among triatomic molecules has been demonstrated in their bond angles (Fig. 1) and heats of atomization (Figs. 9-12). The data accumulated but not included in this report could also be used to display periodicity among the bond lengths. The  $v_1$  values in Table 3 which were not found in [11] or [12], and which have usefully small error measures, could be of use in a visible-light search for free triatomic molecules in interstellar space. There exists a NIST data base containing high-precision long-wavelength spectral features, but for a limited number of triatomic molecules [17]

As explained in Section 4.2, the failure of Fig. 8 to show a completely filled molecular subspace is due to the absence of so many molecules in [13 and 14] and to the failure of many of the computations.

## 7. Acknowledgements

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