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NOTE

FURTHER DUNHAM ENERGY COEFFICIENTS OF DIATOMIC MOLECULES

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Abstract—Expressions are given for the Dunham energy coefficients Y_{33} and Y_{42} in terms of the potential energy coefficients a_i, for diatomic molecules. Their use is briefly discussed.

CALCULATIONS

In previous papers,[1–4] the leading terms of the Dunham energy coefficients (Y_{ij}) used in:

$$E_{vJ} = \sum_{i,j=0} Y_{ij}\left(v+\frac{1}{2}\right)^i (J^2+J)^j$$

were obtained for $i+j \leq 6$, except for Y_{33} and Y_{42}. Because of observations for increasing ranges of vibration–rotation spectra of diatomic molecules (e.g. up to $v=7$ of HBr[5] and HI[6]) and increasing precision of measurements, it is essential to have expressions for Y_{33} and Y_{42}, whether the wavenumbers of the spectral lines are fitted directly to either the Y_{ij} or to the potential energy coefficients[7] a_i such as

$$V(X) = a_0X^2\left(1+\sum_{i=1} a_iX^i\right), \quad X=(R-R_e)/R_e.$$

The following expressions for Y_{33} and Y_{42} have been derived, according to previously used methods:[1,4]

$$\begin{aligned}
Y_{33} = \frac{B_e^8}{\omega_e^7}\Bigg[&\frac{12620205}{16}(a_1^7+3\,a_1^6) - 3323565\,a_1^5a_2 + \frac{69039945}{16}a_1^5 - 7743600\,a_1^4a_2 \\
&+ 1827450\,a_1^4a_3 + \frac{95088015}{16}a_1^4 + 3733845\,a_1^3a_2^2 - \frac{20723535}{2}a_1^3a_2 + 3761550\,a_1^3a_3 \\
&- 908520\,a_1^3a_4 + 6426360\,a_1^3 + 5694975\,a_1^2a_2^2 - 2787900\,a_1^2a_2a_3 - \frac{19195605}{2}a_1^2a_2 \\
&+ 4252725\,a_1^2a_3 - 1568160\,a_1^2a_4 + 388080\,a_1^2a_5 + 5437035\,a_1^2 - 959640\,a_1a_2^3 \\
&+ 4167405\,a_1a_2^2 - 3128400\,a_1a_2a_3 + 803280\,a_1a_2a_4 - 5826240\,a_1a_2 + 397000\,a_1a_3^2 \\
&+ 3025650\,a_1a_3 - 1338660\,a_1a_4 + 498960\,a_1a_5 - 129920\,a_1a_6 + 3342720\,a_1 \\
&- 542520\,a_2^3 + 417200\,a_2^2a_3 + 1429155\,a_2^2 - 1268700\,a_2a_3 + 511920\,a_2a_4 - 137760\,a_2a_5 \\
&- 1786140\,a_2 + 243000\,a_3^2 - 135200\,a_3a_4 + 1048800\,a_3 - 551220\,a_4 + 236040\,a_5 \\
&- 94080\,a_6 + 26880\,a_7 + 1093920\Bigg];
\end{aligned}$$

$$Y_{42}=\frac{B_e^7}{\omega_e^6}\Big[-\frac{65633085}{128}(a_1^8+2a_1^7)+\frac{83937105}{32}a_1^6a_2-\frac{12154275}{8}a_1^6+4182570\,a_1^5a_2$$
$$-\frac{50763825}{32}a_1^5a_3-\frac{14263515}{8}a_1^5-\frac{31570875}{8}a_1^4a_2^2+\frac{77753025}{16}a_1^4a_2$$
$$-\frac{36821925}{16}a_1^4a_3+\frac{14170275}{16}a_1^4a_4-\frac{6983775}{4}a_1^4-\frac{17628975}{4}a_1^3a_2^2$$
$$+\frac{14145075}{4}a_1^3a_2a_3+\frac{8385075}{2}a_1^3a_2-\frac{4825125}{2}a_1^3a_3+1113750\,a_1^3a_4-444150\,a_1^3a_5$$
$$-1454175\,a_1^3+\frac{3497445}{2}a_1^2a_2^3-\frac{13441275}{4}a_1^2a_2^2+3220425\,a_1^2a_2a_3-\frac{2665575}{2}a_1^2a_2a_4$$
$$+\frac{5413725}{2}a_1^2a_2-\frac{2683725}{4}a_1^2a_3^2-\frac{3546825}{2}a_1^2a_3+986850\,a_1^2a_4-455175\,a_1^2a_5$$
$$+191940\,a_1^2a_6-\frac{3913065}{4}a_1^2+979020\,a_1a_2^3-\frac{2621325}{2}a_1a_2^2a_3-1564200\,a_1a_2^2$$
$$+1866000\,a_1a_2a_3-849600\,a_1a_2a_4+377580\,a_1a_2a_5+1243140\,a_1a_2-447300\,a_1a_3^2$$
$$+385680\,a_1a_3a_4-882000\,a_1a_3+543840\,a_1a_4-310800\,a_1a_5+141120\,a_1a_6$$
$$-64260\,a_1a_7-493500\,a_1-108780\,a_2^4+251310\,a_2^3-374175\,a_2^2a_3+188115\,a_2^2a_4$$
$$-316950\,a_2^2+184365\,a_2a_3^2+481290\,a_2a_3-262200\,a_2a_4+115920\,a_2a_5$$
$$-62160\,a_2a_6+262905\,a_2-153300\,a_3^2+130320\,a_3a_4-62160\,a_3a_5$$
$$-240660\,a_3-32580\,a_4^2+138300\,a_4-93660\,a_5+54600\,a_6-22680\,a_7$$
$$+12600\,a_8-126420\Big].$$

These expressions involve potential energy coefficients a_i up to $i=7$ for Y_{33} and $i=8$ for Y_{42}. Using the values of a_i obtained for HBr[7] and HI[8] from an iterative process, we have calculated the following values of the energy coefficients: for HBr,

$$Y_{33}=(-9.3\pm3.8)\times10^{-12}\,\text{cm}^{-1},\quad Y_{42}=(-1.7\pm2.4)\times10^{-9}\,\text{cm}^{-1};$$

for HI,

$$Y_{33}=(-2.1\pm5)\times10^{-13}\,\text{cm}^{-1},\quad Y_{42}=(3.73\pm0.38)\times10^{-9}\,\text{cm}^{-1}.$$

The indicated standard deviations reflect corresponding inaccuracies in a_i through error propagation.[9] The spectra for the $6\leftarrow0$ and $7\leftarrow0$ transitions had a precision of $\simeq0.03\,\text{cm}^{-1}$, whereas later measurements[8] led to improved precision of $\simeq0.003\,\text{cm}^{-1}$. When the $6\leftarrow0$ and $7\leftarrow0$ bands are remeasured with the better precision, the a_i and the predicted Y_{lj} derived from them will be similarly improved. Future measurements may yield accurate experimental values of Y_{33} and Y_{42}, in which case the above expressions may be used both for comparisons to check consistency of the analysis and the effect of truncation of power series.[9]

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