# Interstellar Chemistry: A Strategy for Detecting Polycyclic Aromatic Hydrocarbons in Space

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## Centrifugal Distortion Constants

The statistical weights for the $K$ states of corannulene were determined using the analysis of Weber.[1] Corannulene ($C_{5v}$) has atoms of type 5 in Table I of Weber.[1] Using Eq. (3) with $h$ = 10 (order of the group), Eqs. (4), (8), and (9) afford values for $\chi_S(R)$, and group theory analysis affords values for $\chi_G^{\alpha}(R)$.[2] The resulting $m_\alpha$ values are: $m(A_1) = 120$; $m(A_2) = 88$; $m(E_1) = m(E_2) = 204$. Then from the first column of Table V [1] for the $A_1$ ro-vibronic ground state:

| ***K*** | ***weight*** |
|---|---|
| 0 | $m(A_1) + m(A_2) = 208$ |
| 5p = 5, 10, ... | $2[m(A_1) + m(A_2)] = 416$ |
| 5p ± 1 = 1, 4, 6, 9, 11, ... | $2m(E_1) = 408$ |
| 5p ± 2 = 2, 3, 7, 8, 12, ... | $2m(E_2) = 408$ |

Thus, the weighting of the $K = 0$ state is about half of all the other $K$ states, and the relative magnitudes of the transition matrix elements follow the formula $1 - [K^2 / (J + 1)^2]$.

The analysis reveals that corannulene displays three symmetry species ($A_1 + A_2$), $E_1$, and $E_2$, and cooling in the beam expansion might populate only the states available with energies up to the order of kT. In the case that $D_{JK}$ is extremely small, the analysis is straightforward and the determined constants are $B$ and $D_J$. In the case that $D_{JK}$ is not small, the proper determination of $D_J$ and $D_{JK}$ becomes problematic. If $D_{JK}$ is not small, the value determined for $D_J$ is just an effective value, since the shift attributed to $D_J$ might be caused by the population of higher $K$ states (and depopulation of lower $K$ states) as they become available with higher $J$. In the extreme case, only the three highest $K$ states are populated after the transfer during the supersonic expansion. (If $D_{JK}$ is sufficiently small, however, one would still see only one line in any $J \rightarrow J + 1$ transition). If the population transfer is not complete, more $K$ states would be populated, but the "mean" $K$-value would not be zero.  Most likely, $K$ will be a function of $J$, e.g. $K = J - \mathrm{X}$ with $J^2 > (J - X)^2 > \frac{kT}{C-B} + J^2 > 0$, since states with a relative energy beyond the order of kT will essentially not be populated (e.g. for $J$ levels with $J^2 > \frac{kT}{B-C}$ the population of the $K = 0$ state will decrease significantly; i.e. $J > 14$ assuming a beam temperature of 2.5 K). Irrespective of whether or not population transfer is complete, a simple interpretation of this situation in terms of $D_J$ and $D_{JK}$ is not possible.  In such a case, the value of $D_J$ is just as speculative as $D_{JK}$, since it is not easily possible to distinguish in a fit between $D_J \times J^2 (J + 1)^2$ and $D_{JK} \times J (J + 1) K^2$ approximately equal to $D_{JK} \times J (J + 1)(J - \mathrm{X})^2$.

The Stark effect measurements, however, permit a definite statement on $D_J$.  From the Stark measurements, the $K = 0$ line position was extrapolated to zero-field conditions.  Indeed, the extrapolated line coincides with the measured zero-field line position (Fig 4). This indicates the absence of a line shift arising from a mixture of different overlapping $K$-states, which confirms the small magnitude of $D_{JK}$.  We therefore conclude that the line position for higher $J$-transitions is not affected by a mix of overlapping $K$-states.

From the line width at half maximum intensity for the highest frequency transition observed, a value of 0.0023 kHz for $D_{JK}$ is determined as an upper limit to the splitting from $K = 0$ to $K = 18$.  This limit is half of the value of $D_J$.  The upper limit for $D_{JK}$ should probably be increased somewhat, since the highest $K$ values are likely too weak to observe in the laboratory spectrum.  In the end, extrapolation of the transition frequencies to the mm range (e.g. 75-100 GHz), as well as conclusions from the mm survey data, should be considered with due caution.

**Corannulene Bowl Inversion Process**

Inversion along the c-axis (dipolar axis) would provide two levels for each J state. Transitions from J'' to J' would go from the bottom level in the lower state (J'') to the upper level in the upper state (J'), and vice versa for the other two levels. Thus, the transitions go across the inversion splitting and the observed frequency splitting (if it happened) would be twice the inversion frequency. The narrowest linewidth measured in the current study is 9 kHz, which places an upper limit to the inversion frequency of 5 kHz at the temperature of the measurement (< 2 K). (The rotational temperature in the supersonic expansion is estimated to be 1-2 K). From comparison with other systems, the low inversion frequency (< 5 kHz) seems reasonable for a large reduced mass tunneling through a barrier of 10.2 kcal/mol (measured for an analog of corannulene by dynamic NMR spectroscopy.[3]) Extrapolation of the measured rate to temperatures below 100 K predicts a vanishingly low rate of inversion via a classical, thermally-activated process. The absence of inversion splittings in the laboratory rotational spectra has no implication regarding astronomical observations, particularly for hot sources, which have broad lines. Dark clouds have narrower lines, which are, nevertheless, comparable to the 9 kHz width observed in Hannover.

**References**


(1) Weber, A. *J. Chem. Phys.* **1982**, *76*, 3694-3698.

(2) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; Dover: New York, 1955.

(3) Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 1920-1921.

**Table S1.** Calculated and Measured Rotational Transitions of Corannulene ($C_{20}H_{10}$).

| J' - J" | Calculated Frequency [MHz] | uncertainty (2 σ) | Measured Frequency [MHz] | uncertainty (1 σ) | Energy of Lower State [$cm^{-1}$] |
|---|---|---|---|---|---|
| 1 - 0 | 1019.6854 | ( 1) | | | 0.000 |
| 2 - 1 | 2039.3706 | ( 1) | | | 0.034 |
| 3 - 2 | 3059.0556 | ( 2) | | | 0.102 |
| 4 - 3 | 4078.7404 | ( 2) | | | 0.204 |
| 5 - 4 | 5098.4247 | ( 2) | 5098.4246 | ( 5) | 0.340 |
| 6 - 5 | 6118.1084 | ( 3) | 6118.1081 | ( 5) | 0.510 |
| 7 - 6 | 7137.7916 | ( 3) | 7137.7916 | ( 5) | 0.714 |
| 8 - 7 | 8157.4740 | ( 3) | 8157.4739 | ( 5) | 0.952 |
| 9 - 8 | 9177.1556 | ( 3) | 9177.156 | ( 2) | 1.224 |
| 10 - 9 | 10196.8363 | ( 4) | 10196.838 | ( 2) | 1.531 |
| 11 - 10 | 11216.5159 | ( 4) | 11216.517 | ( 2) | 1.871 |
| 12 - 11 | 12236.1943 | ( 4) | 12236.197 | ( 2) | 2.245 |
| 13 - 12 | 13255.8715 | ( 5) | 13255.872 | ( 2) | 2.653 |
| 14 - 13 | 14275.5473 | ( 6) | 14275.549 | ( 2) | 3.095 |
| 15 - 14 | 15295.2217 | ( 7) | 15295.222 | ( 2) | 3.571 |
| 16 - 15 | 16314.8945 | ( 8) | 16314.894 | ( 2) | 4.082 |
| 17 - 16 | 17334.5657 | ( 10) | 17334.564 | ( 2) | 4.626 |
| 18 - 17 | 18354.2350 | ( 12) | 18354.234 | ( 2) | 5.204 |
| 19 - 18 | 19373.9025 | ( 15) | 19373.903 | ( 2) | 5.816 |
| 20 - 19 | 20393.5680 | ( 18) | | | 6.462 |
| 21 - 20 | 21413.2314 | ( 21) | | | 7.143 |
| 22 - 21 | 22432.8926 | ( 25) | | | 7.857 |
| 23 - 22 | 23452.5515 | ( 29) | | | 8.605 |
| 24 - 23 | 24472.2080 | ( 33) | | | 9.388 |
| 25 - 24 | 25491.8619 | ( 39) | | | 10.204 |
| 26 - 25 | 26511.5133 | ( 44) | | | 11.054 |
| 27 - 26 | 27531.1620 | ( 50) | | | 11.939 |
| 28 - 27 | 28550.8078 | ( 57) | | | 12.857 |
| 29 - 28 | 29570.4507 | ( 64) | | | 13.809 |
| 30 - 29 | 30590.0906 | ( 71) | | | 14.796 |
| 31 - 30 | 31609.7273 | ( 79) | | | 15.816 |
| 32 - 31 | 32629.3608 | ( 88) | | | 16.870 |
| 33 - 32 | 33648.9910 | ( 97) | | | 17.959 |
| 34 - 33 | 34668.6177 | ( 107) | | | 19.081 |
| 35 - 34 | 35688.2408 | ( 118) | | | 20.238 |
| 36 - 35 | 36707.8603 | ( 129) | | | 21.428 |
| 37 - 36 | 37727.4760 | ( 141) | | | 22.652 |
| 38 - 37 | 38747.0879 | ( 153) | | | 23.911 |
| 39 - 38 | 39766.6957 | ( 166) | | | 25.203 |
| 40 - 39 | 40786.2995 | ( 180) | | | 26.530 |

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|---|---|---|
| 41 - 40 | 41805.8992 ( 195) | 27.890 |
| 42 - 41 | 42825.4945 ( 211) | 29.285 |
| 43 - 42 | 43845.0854 ( 227) | 30.713 |
| 44 - 43 | 44864.6719 ( 244) | 32.176 |
| 45 - 44 | 45884.2537 ( 262) | 33.672 |
| 46 - 45 | 46903.8309 ( 280) | 35.203 |
| 47 - 46 | 47923.4032 ( 300) | 36.767 |
| 48 - 47 | 48942.9706 ( 320) | 38.366 |
| 49 - 48 | 49962.5330 ( 341) | 39.999 |
| 50 - 49 | 50982.0903 ( 363) | 41.665 |
| 51 - 50 | 52001.6424 ( 387) | 43.366 |
| 52 - 51 | 53021.1891 ( 411) | 45.100 |
| 53 - 52 | 54040.7304 ( 436) | 46.869 |
| 54 - 53 | 55060.2661 ( 461) | 48.671 |
| 55 - 54 | 56079.7962 ( 488) | 50.508 |
| 56 - 55 | 57099.3205 ( 516) | 52.379 |
| 57 - 56 | 58118.8390 ( 545) | 54.283 |
| 58 - 57 | 59138.3516 ( 575) | 56.222 |
| 59 - 58 | 60157.8580 ( 607) | 58.195 |
| 60 - 59 | 61177.3583 ( 639) | 60.201 |
| 61 - 60 | 62196.8524 ( 672) | 62.242 |
| 62 - 61 | 63216.3400 ( 706) | 64.317 |
| 63 - 62 | 64235.8212 ( 742) | 66.425 |
| 64 - 63 | 65255.2957 ( 779) | 68.568 |
| 65 - 64 | 66274.7636 ( 817) | 70.745 |
| 66 - 65 | 67294.2247 ( 856) | 72.955 |
| 67 - 66 | 68313.6789 ( 896) | 75.200 |
| 68 - 67 | 69333.1261 ( 938) | 77.479 |
| 69 - 68 | 70352.5662 ( 981) | 79.791 |
| 70 - 69 | 71371.9991 ( 1025) | 82.138 |
| 71 - 70 | 72391.4246 ( 1070) | 84.519 |
| 72 - 71 | 73410.8427 ( 1117) | 86.934 |
| 73 - 72 | 74430.2533 ( 1165) | 89.382 |
| 74 - 73 | 75449.6563 ( 1214) | 91.865 |
| 75 - 74 | 76469.0515 ( 1265) | 94.382 |
| 76 - 75 | 77488.4389 ( 1317) | 96.932 |
| 77 - 76 | 78507.8183 ( 1370) | 99.517 |
| 78 - 77 | 79527.1897 ( 1425) | 102.136 |
| 79 - 78 | 80546.5530 ( 1482) | 104.789 |
| 80 - 79 | 81565.9079 ( 1540) | 107.475 |
| 81 - 80 | 82585.2545 ( 1599) | 110.196 |
| 82 - 81 | 83604.5927 ( 1660) | 112.951 |
| 83 - 82 | 84623.9223 ( 1722) | 115.740 |
| 84 - 83 | 85643.2432 ( 1786) | 118.562 |
| 85 - 84 | 86662.5553 ( 1851) | 121.419 |
| 86 - 85 | 87681.8585 ( 1918) | 124.310 |
| 87 - 86 | 88701.1527 ( 1987) | 127.235 |
| 88 - 87 | 89720.4379 ( 2057) | 130.193 |
| 89 - 88 | 90739.7138 ( 2129) | 133.186 |
| 90 - 89 | 91758.9804 ( 2202) | 136.213 |

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|---|---|---|---|
| 91 - 90 | 92778.2376 | ( 2277) | 139.274 |
| 92 - 91 | 93797.4854 | ( 2354) | 142.368 |
| 93 - 92 | 94816.7234 | ( 2432) | 145.497 |
| 94 - 93 | 95835.9518 | ( 2512) | 148.660 |
| 95 - 94 | 96855.1703 | ( 2594) | 151.857 |
| 96 - 95 | 97874.3790 | ( 2678) | 155.087 |
| 97 - 96 | 98893.5775 | ( 2763) | 158.352 |
| 98 - 97 | 99912.7660 | ( 2850) | 161.651 |
| 99 - 98 | 100931.9441 | ( 2939) | 164.984 |
| 100 - 99 | 101951.1120 | ( 3030) | 168.350 |
| 101 - 100 | 102970.2693 | ( 3123) | 171.751 |
| 102 - 101 | 103989.4162 | ( 3217) | 175.186 |
| 103 - 102 | 105008.5523 | ( 3314) | 178.654 |
| 104 - 103 | 106027.6777 | ( 3412) | 182.157 |
| 105 - 104 | 107046.7922 | ( 3512) | 185.694 |
| 106 - 105 | 108065.8957 | ( 3614) | 189.265 |
| 107 - 106 | 109084.9882 | ( 3719) | 192.869 |
| 108 - 107 | 110104.0695 | ( 3825) | 196.508 |
| 109 - 108 | 111123.1394 | ( 3933) | 200.181 |
| 110 - 109 | 112142.1980 | ( 4043) | 203.887 |
| 111 - 110 | 113161.2451 | ( 4155) | 207.628 |
| 112 - 111 | 114180.2806 | ( 4269) | 211.403 |
| 113 - 112 | 115199.3043 | ( 4385) | 215.211 |
| 114 - 113 | 116218.3163 | ( 4504) | 219.054 |
| 115 - 114 | 117237.3163 | ( 4624) | 222.931 |
| 116 - 115 | 118256.3043 | ( 4746) | 226.841 |
| 117 - 116 | 119275.2802 | ( 4871) | 230.786 |
| 118 - 117 | 120294.2438 | ( 4998) | 234.764 |
| 119 - 118 | 121313.1952 | ( 5127) | 238.777 |
| 120 - 119 | 122332.1340 | ( 5258) | 242.823 |
| 121 - 120 | 123351.0604 | ( 5392) | 246.904 |
| 122 - 121 | 124369.9740 | ( 5527) | 251.019 |
| 123 - 122 | 125388.8749 | ( 5665) | 255.167 |
| 124 - 123 | 126407.7630 | ( 5805) | 259.350 |
| 125 - 124 | 127426.6381 | ( 5948) | 263.566 |
| 126 - 125 | 128445.5001 | ( 6092) | 267.817 |
| 127 - 126 | 129464.3490 | ( 6239) | 272.101 |
| 128 - 127 | 130483.1846 | ( 6389) | 276.420 |
| 129 - 128 | 131502.0067 | ( 6541) | 280.772 |
| 130 - 129 | 132520.8155 | ( 6695) | 285.158 |
| 131 - 130 | 133539.6106 | ( 6851) | 289.579 |
| 132 - 131 | 134558.3920 | ( 7010) | 294.033 |
| 133 - 132 | 135577.1596 | ( 7171) | 298.522 |
| 134 - 133 | 136595.9133 | ( 7335) | 303.044 |
| 135 - 134 | 137614.6530 | ( 7502) | 307.600 |
| 136 - 135 | 138633.3786 | ( 7670) | 312.191 |
| 137 - 136 | 139652.0900 | ( 7842) | 316.815 |
| 138 - 137 | 140670.7870 | ( 8016) | 321.473 |
| 139 - 138 | 141689.4696 | ( 8192) | 326.166 |
| 140 - 139 | 142708.1377 | ( 8371) | 330.892 |

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|---|---|---|---|
| 141 - 140 | 143726.7912 | ( 8552) | 335.652 |
| 142 - 141 | 144745.4299 | ( 8736) | 340.446 |
| 143 - 142 | 145764.0538 | ( 8923) | 345.275 |
| 144 - 143 | 146782.6627 | ( 9112) | 350.137 |
| 145 - 144 | 147801.2565 | ( 9304) | 355.033 |
| 146 - 145 | 148819.8352 | ( 9499) | 359.963 |
| 147 - 146 | 149838.3987 | ( 9697) | 364.927 |
| 148 - 147 | 150856.9467 | ( 9897) | 369.925 |
| 149 - 148 | 151875.4793 | ( 10099) | 374.957 |
| 150 - 149 | 152893.9963 | ( 10305) | 380.023 |
| 151 - 150 | 153912.4977 | ( 10513) | 385.123 |
| 152 - 151 | 154930.9832 | ( 10724) | 390.257 |
| 153 - 152 | 155949.4529 | ( 10938) | 395.425 |
| 154 - 153 | 156967.9065 | ( 11155) | 400.627 |
| 155 – 154 | 157986.3441 | ( 11375) | 405.863 |