# Linewidths and temperature exponents of CH$_3$CN-N$_2$

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## ABSTRACT

Calculations of nitrogen-broadening coefficients and their temperature exponents for methyl cyanide lines at the room temperature using semi-empirical method are presented. They were performed for wide ranges of rotational quantum numbers $J$ and $K$ requested for atmospheric applications: $J$ from 0 till 70 and $K$ from 0 till 20. The temperature exponents were calculated for every mentioned line. Extensive line lists are provided for the Earth and Titan atmosphere temperature ranges.

**Keywords:** broadening coefficient, temperature exponent, Earth and Titan atmospheres, spectroscopy, intermolecular interactions

Acetonitrile (methyl cyanide) CH$_3$CN is the simplest organic nitrile, produced by biomass burning and industrial processes (long-living pollutant). It is important for astrophysical applications, for example, for the upper stratosphere of Titan, comets and interstellar medium study as well.

The goal of the present work is to report the theoretical data on CH$_3$CN–N$_2$ broadening coefficients and their temperature dependences for large intervals of rotational quantum numbers $J$ and $K$ ($0 \leq J \leq 70$, $K \leq 20$) requested by spectroscopic databases. Since the semi-classical approaches do not work well for the self-broadening of lines of molecules with large dipole moments (CH$_3$CN[1], CH$_3$Cl[2,3], CH$_3$Br[4], we use a semi-empirical (SE) method[5] which has proved its efficiency for highly polar molecules of atmospheric interest such as H$_2$O[5,6], O$_3$[7], CH$_3$Cl[8].

The most of articles dedicated to CH$_3$CN-N$_2$ line widths referred to the pure rotational absorption band[9-12]. Only one work[13] reports methyl cyanide line broadening in the $\nu_4$ band. In addition, this work[13] dedicated to the (parallel) $\nu_4$ band gives the most complete set of experimental CH$_3$CN-N$_2$ line-broadening parameters: over 700 mid-infrared transitions ($J \leq 48$, $K \leq 10$) in both $P$- and $R$-branches.

To calculate self-broadened halfwidths of CH$_3$CN lines we applied the semi-empirical impact-approximation approach[5] which incorporates empirical corrections into the semi-classical Robert-Bonamy formalism[14] in order to simplify it to an Anderson-type[15] form.

In the SE method the halfwidth associated with the radiative transition $f \leftarrow i$ is defined by

$$\gamma_{if} = \frac{n}{c} \sum_r \rho(r) \int_0^\infty \upsilon F(\upsilon) d\upsilon \int_0^\infty b \, \mathrm{Re} \, S(b) db, \tag{1}$$

where $n$ and $\rho(r)$ are the density and $r$-level rotational populations of the perturbing molecules, $F(\upsilon)$ is the Maxwell-Boltzmann distribution over relative molecular velocities $\upsilon$, and $S(b)$ is the interruption function determined by the impact parameter $b$. Dividing the inner integral over $b$ into two parts (from 0 to the cut-off parameter $b_0(\upsilon, r, i, f)$ and from

$b_0(\upsilon,r,i,f)$ to $\infty$) and neglecting the third and higher-order terms in the expansion of the scattering matrix, the expression (1) can be rewritten as

$$\gamma_{if} = \frac{n}{c}\sum_r \rho(r)\int_0^\infty \upsilon F(\upsilon)b_0^2(\upsilon,r,i,f)d\upsilon + \sum_{i'l} D^2(ii'|l)P_l(\omega_{ii'}) + \sum_{f'l} D^2(ff'|l)P_l(\omega_{ff'}).\qquad(2)$$

In Eq. (2) the second and third terms depend on the transition strengths $D^2(ii'|l)$ and $D^2(ff'|l)$ as well as on the "efficiency functions" $P_l(\omega_{ii'})$ and $P_l(\omega_{ff'})$ corresponding to the scattering channels $i \to i',\ f \to f'$ in the active molecule for the dipole ($l=1$), quadrupole ($l=2$), etc. transitions. While the transition strengths are (well established) characteristics of the absorbing molecule only, the weighting coefficients $P_l(\omega_{ii'})$ and $P_l(\omega_{ff'})$ are defined by the properties of both colliding molecules and by their interaction (which is much less known):

$$P_l(\omega_{ii'}) = \frac{n}{c}\sum_r \rho(r)\sum_{l',r'} A_{ll'} D^2(rr'|l')F_{ll'}(k_{ii'rr'})\qquad(3)$$

(for the final state the corresponding expression is obtained by replacing the frequencies $\omega_{ii'}$ by $\omega_{ff'}$). Here $A_{ll'}$ are the normalization factors for the resonance functions $f_{ll'}(k_{ii'rr'})$ at $k_{ii'rr'}=0$, $F_{ll'}$ are specific functions dependent on the resonance parameter $k_{ii'rr'}$. Since the coefficients $P_l$ are not known precisely, they are considered as products of the analytical efficiency functions $P_l^{ATC}$ of the ATC theory and frequency-dependent empirical correction factors $C_l$:

$$P_l(\omega_{ii'}) = P_l^{ATC}(\omega_{ii'})C_l(\omega_{ii'}).\qquad(4)$$

The correction factor is chosen in a convenient mathematical form (depending on the considered colliding pair) with a empirical parameters fitted on available measured line widths:

$$C_l(\omega_{jj'}) = \frac{c_1}{c_2\sqrt{J_j}+1}\cdot\frac{1}{c_3(J_j-c_4)^2+1}\qquad(5)$$

and adjusted the model parameters $c_1$–$c_4$ on data[13] for each experimentally accessible $K$-value in $R$-branch (the data for the $R$-branch are more complete and our previous study of the self-broadening case show that the parameters $c_1$–$c_4$ are not branch-sensitive). The set of SE parameters for $K \le 10$ is given in Table 1.

The $c_1$–$c_4$ parameters vary relatively slowly with increasing $K$ due to the smooth $K$-dependences of experimental line widths. Therefore, each SE parameter $c_k$ ($k=1,2,3,4$) was assumed to be a linear function of $K$:

$$c_k = c_k^0 + c_k^1 K.\qquad(6)$$

To test the validity of such modelling we adjusted the eight new parameters on experimental $R$-branch data[13] for $K=1$ and $K=7$ only ($c_1^0=0.4265$, $c_1^1=-0.0165$, $c_2^0=0.06$, $c_2^1=0.01$, $c_3^0=0.001$, $c_3^1=0.0015$, $c_4^0=8$, $c_4^1=1$) and compared the recomputed halfwidths with the previous theoretical values for all experimentally available $K$ ($K=0-10$). Generally, the differences were less than 0.3 %, whereas the number of parameters was reduced from 44 to 8. With this

new $K$-dependent correction factor we also computed the root-mean-square (RMS) deviations of new theoretical results from experimental values[13] in both $R$- and $P$-branches (Table 2).

**Table 1.** SE-model fitting parameters (for $K$-independent correction factor) extracted from experimental values of $N_2$-broadening coefficients of $R$-branch $CH_3CN$ lines[13].

| $K$ | $c_1$ | $c_2$ | $c_3$ | $c_4$ |
|---|---|---|---|---|
| 0 | 0.436 | 0.06 | 0.0010 | 8 |
| 1 | 0.410 | 0.07 | 0.0025 | 9 |
| 2 | 0.390 | 0.08 | 0.0040 | 10 |
| 3 | 0.370 | 0.09 | 0.0055 | 11 |
| 4 | 0.352 | 0.10 | 0.0070 | 12 |
| 5 | 0.335 | 0.11 | 0.0085 | 13 |
| 6 | 0.319 | 0.12 | 0.0100 | 14 |
| 7 | 0.311 | 0.13 | 0.0115 | 15 |
| 8 | 0.292 | 0.14 | 0.0130 | 16 |
| 9 | 0.279 | 0.15 | 0.0145 | 17 |
| 10 | 0.266 | 0.16 | 0.0160 | 18 |

**Table 2.** RMS-deviations ($cm^{-1}$ $atm^{-1}$) of SE broadening coefficients calculated with the $K$-dependent correction factor from experimental data[13].

| $K$ | $R$-branch | $P$-branch |
|---|---|---|
| 0 | 0.0028 | 0.0036 |
| 1 | 0.0042 | 0.0035 |
| 2 | 0.0021 | 0.0016 |
| 3 | 0.0016 | 0.0017 |
| 4 | 0.0021 | 0.0015 |
| 5 | 0.0021 | 0.0012 |
| 6 | 0.0029 | 0.0019 |
| 7 | 0.0029 | 0.0016 |
| 8 | 0.0043 | 0.0030 |
| 9 | 0.0046 | 0.0018 |
| 10 | 0.0065 | 0.0059 |

Typically, the deviations for the $P$-branch are even smaller than the deviations for the $R$-branch which was used for adjusting. It means that similar to the self-broadening case the SE parameters deduced from $R$-branch values can be safely used to calculate the $P$-branch ones. As a result, $N_2$-broadening coefficients of methyl cyanide $^QP$- and $^QR$-branch lines for the reference temperature 296 K were calculated using this 8-parameter correction factor for a huge numbers of rotational quantum numbers ($0 \leq J \leq 70$, $K \leq 20$). Examples for $^QR$-lines with $K = 1$, 6 and $J \leq 36$ can be found in Table 3.

Theoretical $^QR$ broadening coefficients in comparison with experimental data in the pure rotational[11,12] and the $\nu_4$ [13] bands can be seen in Fig. 2 for $K = 1, 4, 7, 10$.

Our computations for the $^QR$- and $^QP$-branches show slightly higher values for the $P$-branch lines at very small $J$ but this difference can be hardly considered as meaningful given the adjusting aspect of our theoretical approach and the use of $R$-branch-fitted parameters for both branches. For $|m|$ greater than ~7 the SE curves are strictly identical for $P$-and $R$-lines, perfectly verifying the well-known empirical relation $\gamma_P(J,K) \approx \gamma_R(J-1,K)$. Therefore, the branch-dependence of $CH_3CN$-$N_2$ line-broadening coefficients can be considered as negligible and the theoretical values calculated for the $R$-branch lines can be easily and safely used for the $P$-branch lines just by replacing $J$ with $J+1$. The absence of any systematic deviation in the ($\gamma_R - \gamma_P$) differences for both calculations and measurements confirms this conclusion.

To obtain the temperature exponents $N$ we computed line widths for two sets of temperatures: 250, 280, 310, 340 K for the terrestrial atmosphere [characterized by the temperature range 200–310 K[16] and 90, 130, 170 K for Titan's atmosphere [featured by the interval 94–170 K[17]]. After that, by the usual expression we extracted two associated sets of

**Table 3.** Example of SE-calculated $N_2$-broadening coefficients $\gamma$ (in cm$^{-1}$atm$^{-1}$) of methyl cyanide $^Q R$-branch lines for $K = 1$, 6 and $J \le 36$ at the reference temperature of 296 K and corresponding temperature exponents $N$ for the Earth's and Titan's temperature intervals. The quoted uncertainties correspond to one standard deviation.

| $J$ | $K$ | $\gamma(296)$ | $N_{Earth}$ | $N_{Titan}$ | $J$ | $K$ | $\gamma(296)$ | $N_{Earth}$ | $N_{Titan}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 0.1709 | 0.839(1) | 0.840(1) | 35 | 1 | 0.1260 | 0.618(5) | 0.70(3) |
| 2 | 1 | 0.1734 | 0.836(1) | 0.829(4) | 36 | 1 | 0.1253 | 0.623(5) | 0.71(2) |
| 3 | 1 | 0.1751 | 0.828(1) | 0.810(6) | 6 | 6 | 0.1497 | 0.792(3) | 0.75(1) |
| 4 | 1 | 0.1761 | 0.816(2) | 0.787(9) | 7 | 6 | 0.1528 | 0.774(4) | 0.72(1) |
| 5 | 1 | 0.1762 | 0.800(3) | 0.76(1) | 8 | 6 | 0.1554 | 0.756(5) | 0.70(1) |
| 6 | 1 | 0.1755 | 0.783(4) | 0.74(1) | 9 | 6 | 0.1572 | 0.737(5) | 0.68(2) |
| 7 | 1 | 0.1742 | 0.765(4) | 0.71(1) | 10 | 6 | 0.1583 | 0.719(6) | 0.66(2) |
| 8 | 1 | 0.1727 | 0.747(5) | 0.69(2) | 11 | 6 | 0.1585 | 0.701(6) | 0.64(2) |
| 9 | 1 | 0.1708 | 0.729(6) | 0.67(2) | 12 | 6 | 0.1578 | 0.685(6) | 0.62(2) |
| 10 | 1 | 0.1687 | 0.711(6) | 0.65(2) | 13 | 6 | 0.1562 | 0.670(6) | 0.61(1) |
| 11 | 1 | 0.1665 | 0.695(6) | 0.63(2) | 14 | 6 | 0.1541 | 0.657(6) | 0.60(1) |
| 12 | 1 | 0.1642 | 0.680(6) | 0.61(2) | 15 | 6 | 0.1521 | 0.645(6) | 0.59(1) |
| 13 | 1 | 0.1618 | 0.665(6) | 0.60(1) | 16 | 6 | 0.1501 | 0.634(6) | 0.58(1) |
| 14 | 1 | 0.1595 | 0.652(6) | 0.59(1) | 17 | 6 | 0.1481 | 0.625(6) | 0.575(9) |
| 15 | 1 | 0.1572 | 0.640(6) | 0.58(1) | 18 | 6 | 0.1462 | 0.617(6) | 0.572(7) |
| 16 | 1 | 0.1549 | 0.630(6) | 0.58(1) | 19 | 6 | 0.1443 | 0.610(5) | 0.572(5) |
| 17 | 1 | 0.1526 | 0.620(6) | 0.571(9) | 20 | 6 | 0.1425 | 0.604(5) | 0.575(3) |
| 18 | 1 | 0.1505 | 0.612(5) | 0.569(7) | 21 | 6 | 0.1408 | 0.601(4) | 0.580(1) |
| 19 | 1 | 0.1484 | 0.606(5) | 0.569(5) | 22 | 6 | 0.1392 | 0.598(4) | 0.586(3) |
| 20 | 1 | 0.1464 | 0.601(5) | 0.572(2) | 23 | 6 | 0.1376 | 0.596(3) | 0.594(6) |
| 21 | 1 | 0.1446 | 0.597(4) | 0.577(1) | 24 | 6 | 0.1361 | 0.594(2) | 0.603(9) |
| 22 | 1 | 0.1428 | 0.595(4) | 0.584(3) | 25 | 6 | 0.1347 | 0.595(1) | 0.61(1) |
| 23 | 1 | 0.1410 | 0.593(3) | 0.592(6) | 26 | 6 | 0.1333 | 0.595(1) | 0.63(2) |
| 24 | 1 | 0.1394 | 0.592(2) | 0.602(9) | 27 | 6 | 0.1319 | 0.595(1) | 0.64(2) |
| 25 | 1 | 0.1378 | 0.592(2) | 0.61(1) | 28 | 6 | 0.1306 | 0.596(1) | 0.65(2) |
| 26 | 1 | 0.1363 | 0.593(1) | 0.63(2) | 29 | 6 | 0.1293 | 0.597(1) | 0.66(2) |
| 27 | 1 | 0.1348 | 0.594(1) | 0.64(2) | 30 | 6 | 0.1281 | 0.597(2) | 0.67(3) |
| 28 | 1 | 0.1334 | 0.595(1) | 0.65(2) | 31 | 6 | 0.1269 | 0.597(2) | 0.67(3) |
| 29 | 1 | 0.1320 | 0.595(2) | 0.66(2) | 32 | 6 | 0.1259 | 0.600(3) | 0.68(3) |
| 30 | 1 | 0.1306 | 0.596(2) | 0.67(3) | 33 | 6 | 0.1251 | 0.606(4) | 0.69(3) |
| 31 | 1 | 0.1294 | 0.596(3) | 0.67(3) | 34 | 6 | 0.1244 | 0.612(5) | 0.70(3) |
| 32 | 1 | 0.1283 | 0.599(4) | 0.68(3) | 35 | 6 | 0.1238 | 0.618(5) | 0.70(3) |
| 33 | 1 | 0.1274 | 0.605(4) | 0.69(3) | 36 | 6 | 0.1232 | 0.623(5) | 0.71(2) |
| 34 | 1 | 0.1267 | 0.612(5) | 0.70(3) | | | | | |

temperature exponents $N$ for the Earth and Titan temperature ranges. These data for the $^Q R$-lines are present in Fig. 4 as functions of the rotational quantum number $J$ for fixed $K$-values. It seen a good agreement of the measured and calculated data.

As a result, the present work completes the previously reported $^Q P$- and $^Q R$-line lists for $CH_3CN$ self-broadening coefficients and associated temperature exponents determined separately for the temperature ranges of Earth and Titan atmospheres. Besides the standard choice of the semi-empirical correction factor with a parametric dependence on $K$ (which requires an extrapolation procedure to get the model parameters sets for high $K$-values non available experimentally), the nitrogen-broadening line widths and their temperature dependences are obtained, in addition, with a

new form of the SE correction factor which contains explicitly the *K*-dependence and enables computations for any *K* with the set of only eight adjusted model parameters. Moreover, the predicted broadening coefficients are very close to recent room-temperature measurements in the pure rotational band, which means that the vibrational dependence of $CH_3CN-N_2$ line widths is rather negligible.
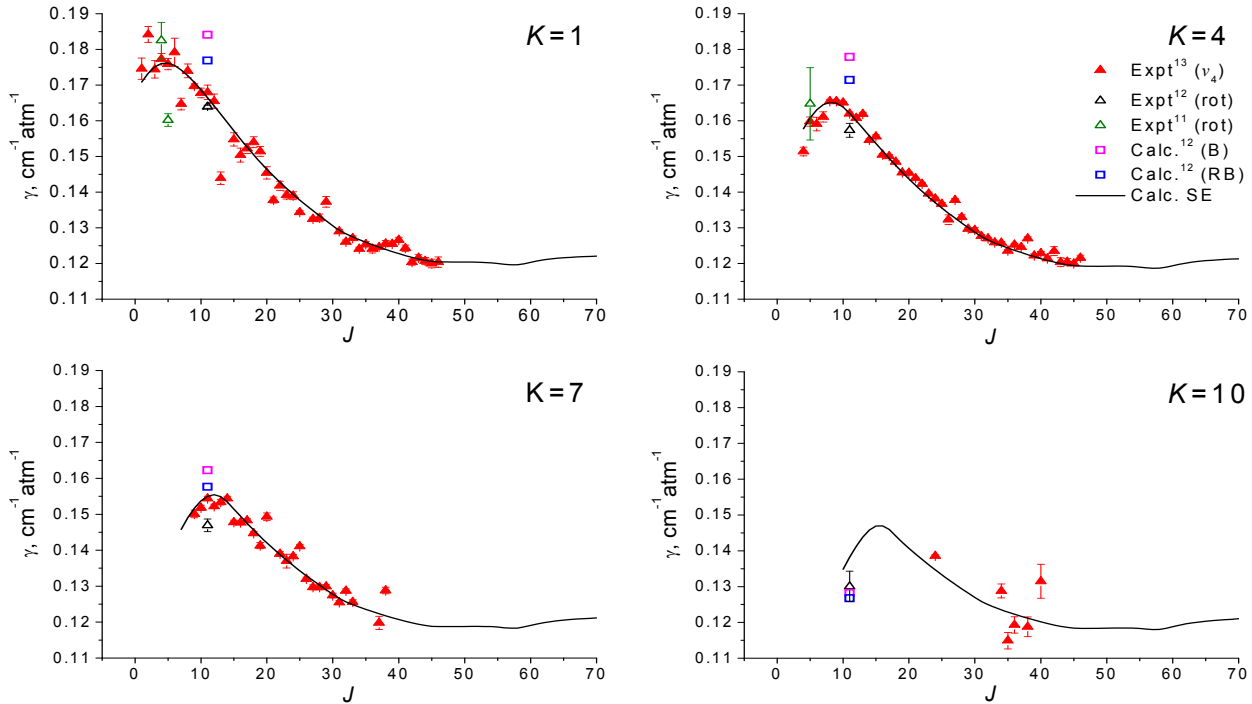


**Fig. 1.** Comparison of semi-empirical room-temperature $CH_3CN-N_2$ $^QR$ line-broadening coefficients with the measurements in the $\nu_4$ [13] and the rotational[11,12] bands; calculations with the Birnbaum (B) and Robert-Bonamy (RB) formalisms [12] are also shown.
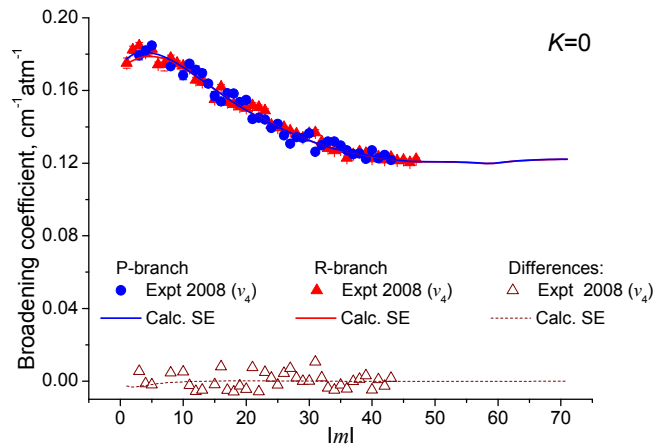


**Fig. 2.** Analysis of branch-dependence for $CH_3CN-N_2$ line-broadening coefficients: SE values computed for $^QP$- and $^QR$-lines (solid curves) are practically identical, in agreement with the experimental data[13] in the $\nu_4$ band (full circles and full triangles, respectively). The differences between *R*- and *P*-values are explicitly shown at the bottom of the figure for both computations and measurements.
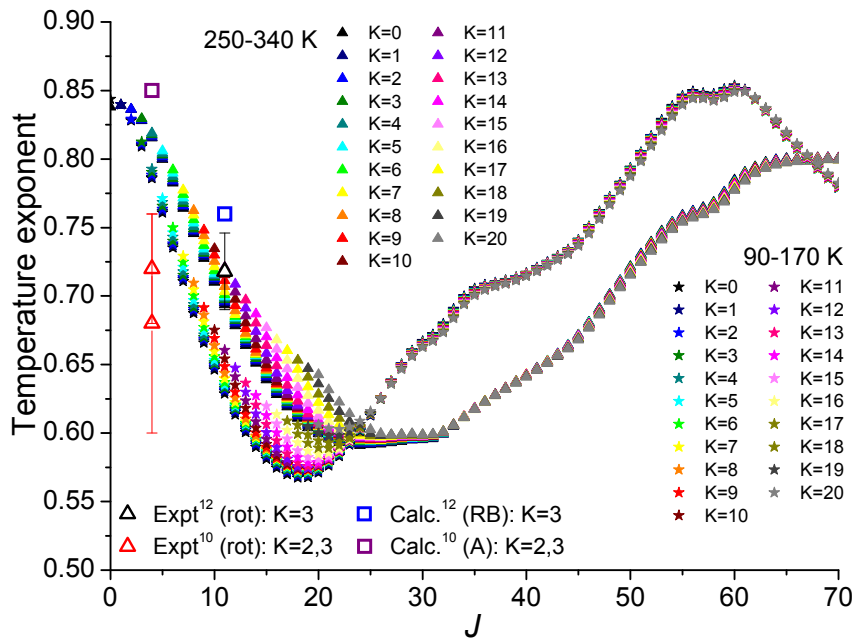
**Fig. 3.** "Earth" and "Titan" sets of SE-calculated temperature-dependence exponents for nitrogen-broadened methyl cyanide lines as functions of rotational quantum number $J$ for $0 \le K \le 20$ and values [10,12].

The temperature exponents deduced from SE-computations assuming the temperature-independence of the adjusting parameters are found to be in a very reasonable agreement with rotational-band experimental data. In addition, they yield a correct prediction of the temperature-dependent rotational $12_3 \leftarrow 11_3$-line widths in the range 236–347 K[12]. This latter fact argues in favor of the validity of our temperature exponents for the Earth atmosphere. For the low temperatures characteristic of Titan atmosphere, no measurements are currently available, so that our $N_{Titan}$ values should be considered as possible estimates.

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