

Vibrational Optical Activity of Inter-Molecular, Overtone and Combination Bands: 2-Chloropropionitrile and α -Pinene

Pavel Michal,^{†*} Radek Čelechovský,[†] Michal Dudka,[†] Josef Kapitán,[†] Milan Vůjtek,[†] Marie Berešová,^{#‡} Jaroslav Šebestík,[‡] Karthick Thangavel,[‡] and Petr Bour^{†*}

[†]*Department of Optics, Palacký University Olomouc, 17. listopadu 12,
77146, Olomouc, Czech Republic*

[#]*Department of Analytical Chemistry, University of Chemistry and Technology, Technická 5,
16628, Prague, Czech Republic*

[‡]*Institute of Organic Chemistry and Biochemistry, Academy of Sciences, Flemingovo náměstí 2,
16610, Prague, Czech Republic*

Content

[**Figure S1.**](#) Unprocessed nitrile vibrational spectra

[**Figure S2.**](#) Unprocessed α -pinene vibrational spectra

[**Figure S3.**](#) The function used for dispersion of the optimization frequency limit

[**Figure S4.**](#) Dependence of the anharmonic force constants on differentiation step

[**Figure S5.**](#) Nitrile Raman and ROA spectra calculated with different methods

[**Figure S6.**](#) Calculated energy dependence of the nitrile on the Ψ angle

[**Figure S7.**](#) Energy as a function of Ψ and ω , and distributions of cluster geometries

[**Figure S8.**](#) Frequency shifts as dependent on Ψ and ω

[**Figure S9.**](#) ROA intensity dependence on Ψ and ω

[**Figure S10.**](#) Angular distribution in nitrile obtained by MD

[**Figure S11.**](#) Example of the AIM analysis of nitrile-nitrile interactions

[**Figure S12.**](#) Nitrile ROA spectra for methanol solution.

[**Figure S13.**](#) Nitrile IR and VCD spectra in the anharmonic region

[**Figure S14.**](#) Raman and ROA spectra of α -pinene, LVCI calculation included.

[**Figure S15.**](#) α -pinene IR and VCD spectra in the anharmonic region

Table S1. Conditions of ROA measurements

Table S2. Nitrile fundamental modes

Table S3. Nitrile combination modes and overtones

Table S4. AIM topological parameters of interacting atoms in nitrile dimers

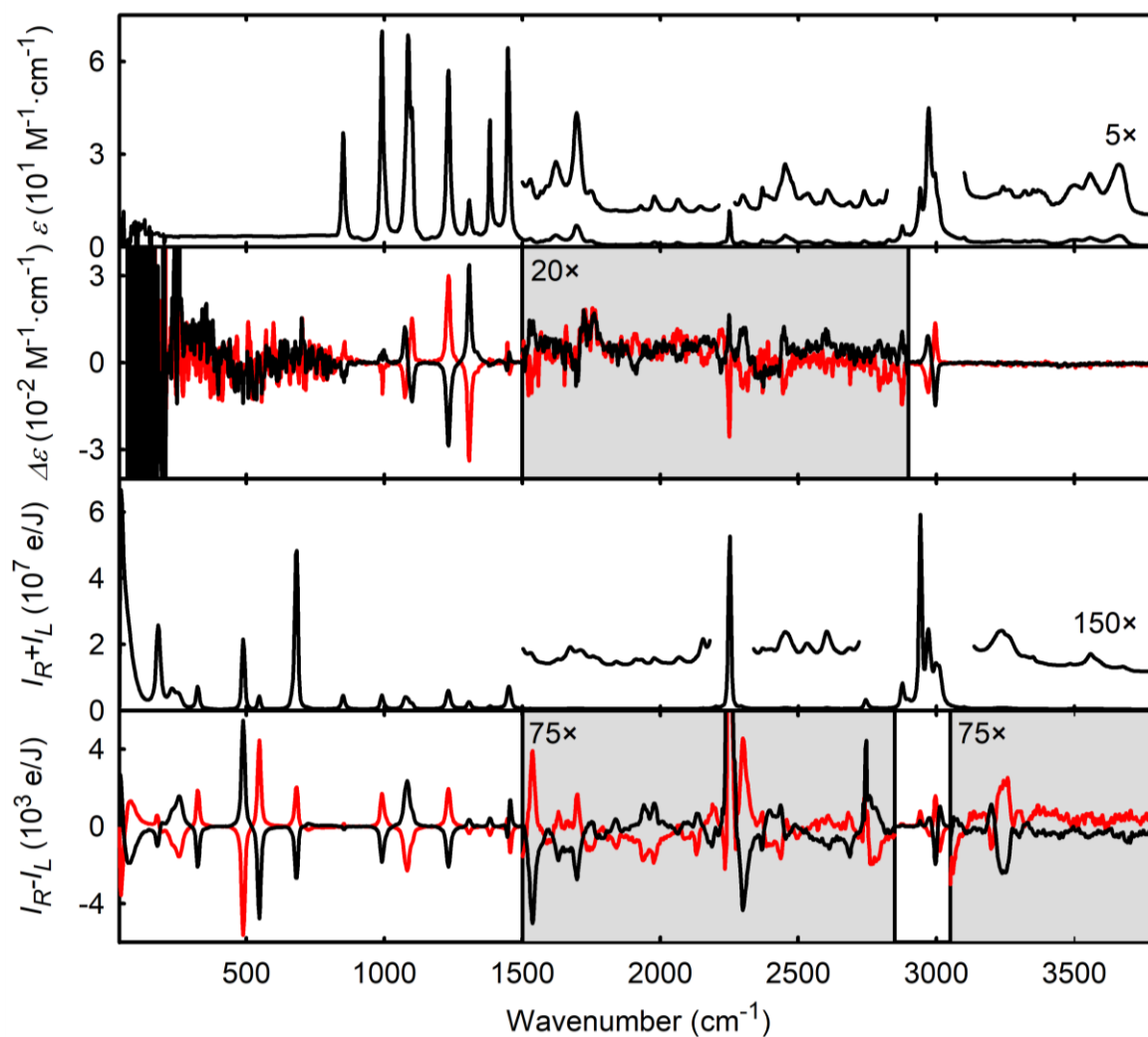


Figure S1. Experimental IR, VCD, Raman and ROA raw spectra of (R-red, S-black) 2-chloropropionitrile; regions of overtone and combination modes are enlarged.

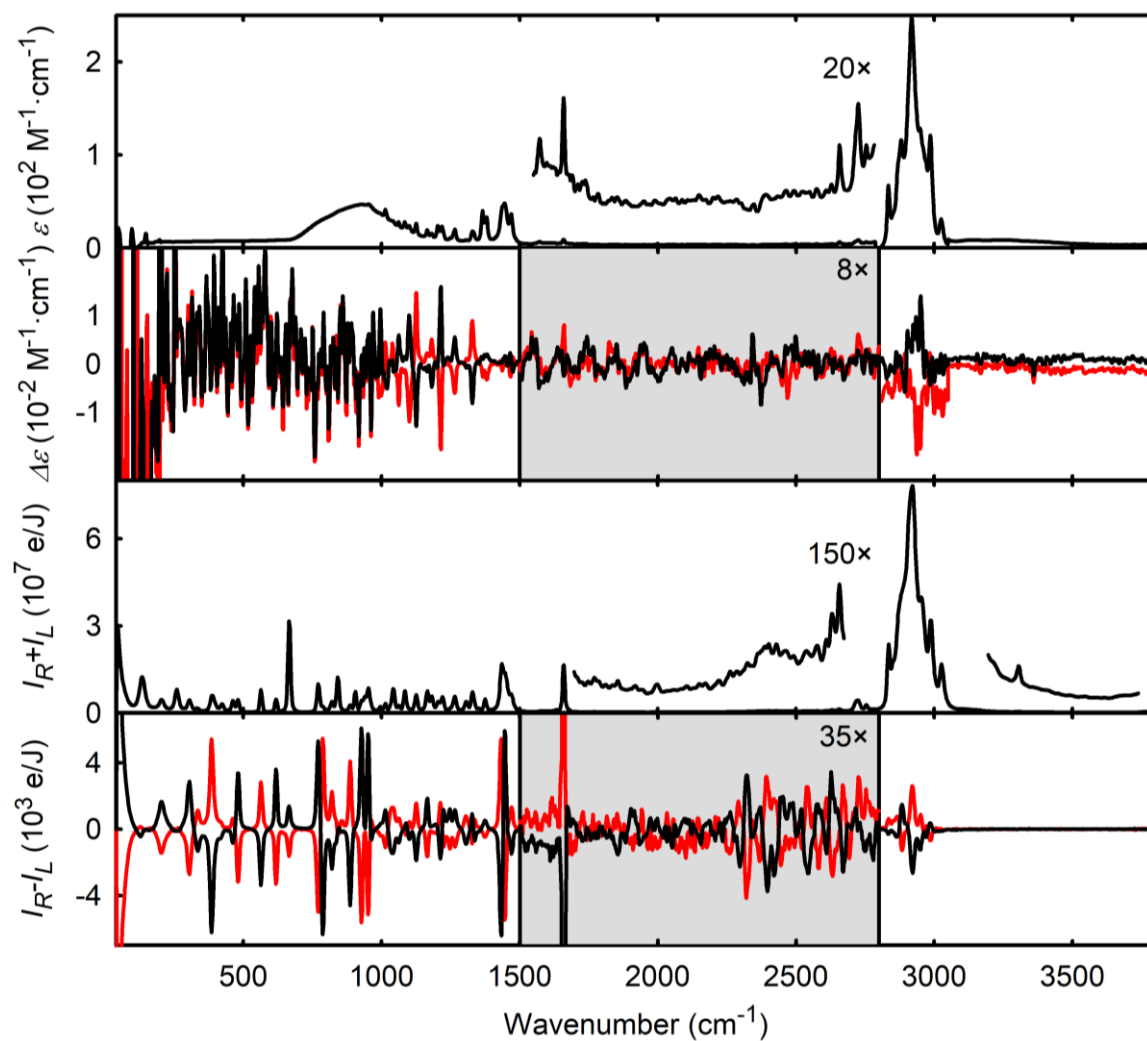


Figure S2. Experimental IR, VCD, Raman and ROA raw spectra of $((+)\text{-red}, (-)\text{-black})$ α -pinene; regions of overtone and combination modes are enlarged.

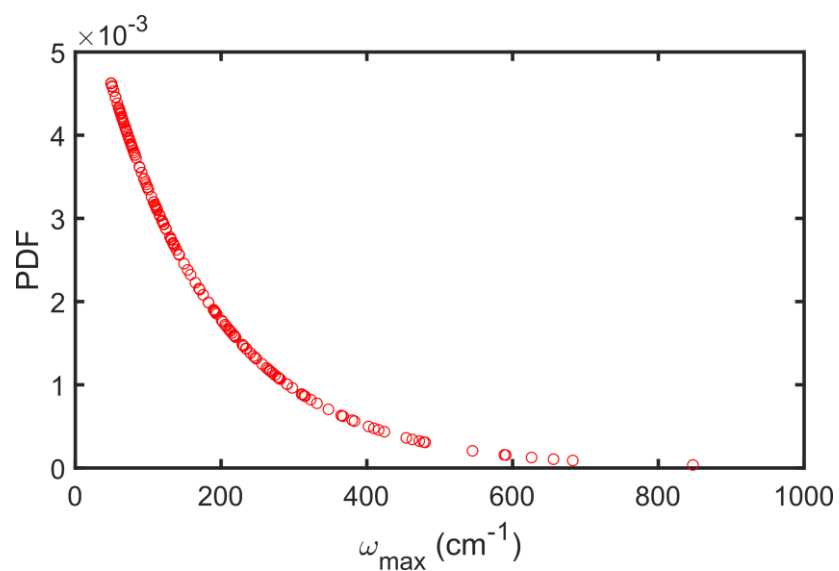


Figure S3. Random exponential function used for the optimization frequency limit for 200 nitrile clusters.

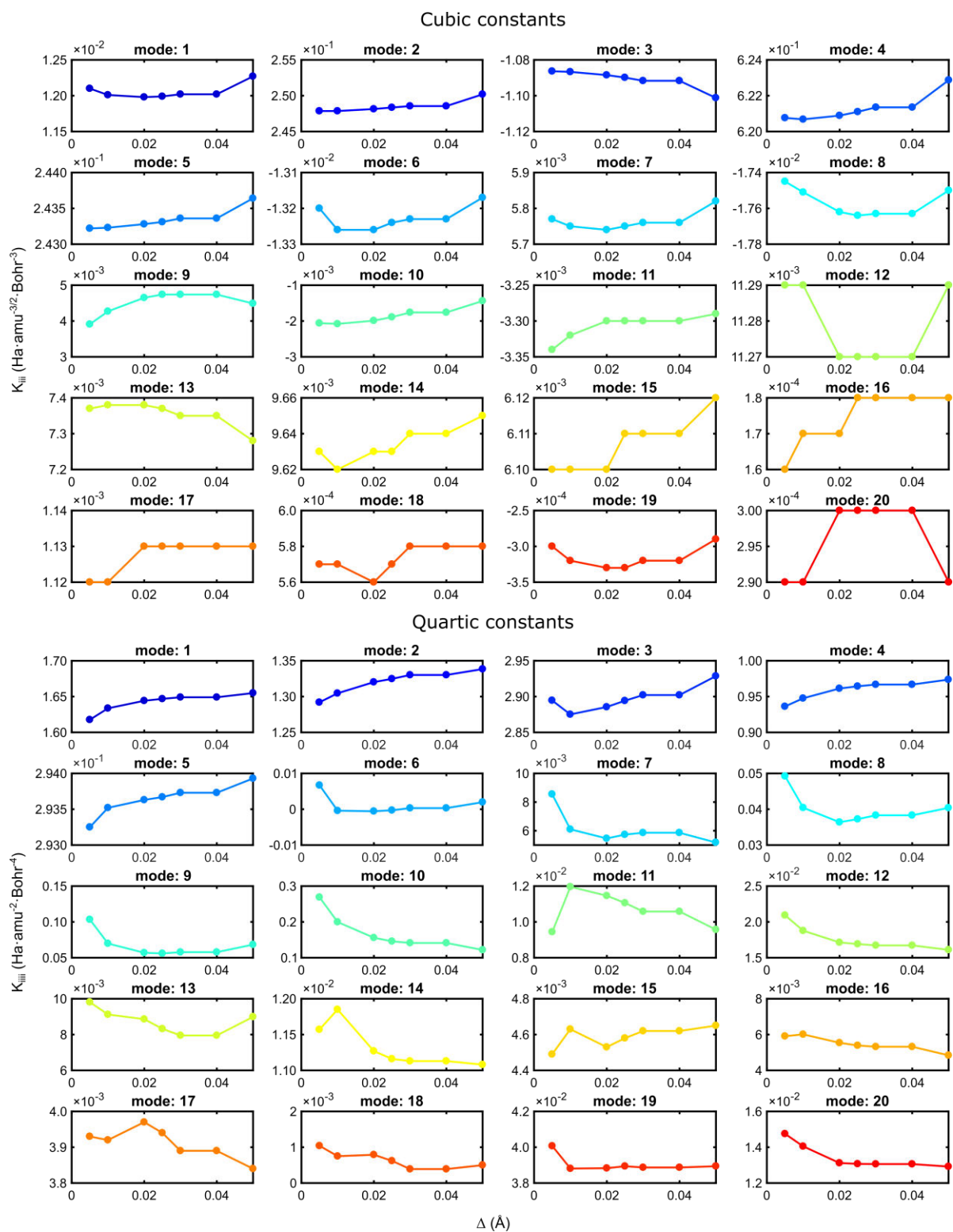


Figure S4. Dependence of calculated cubic and quartic diagonal normal mode nitrile force constants on the size of the numerical differentiation step.

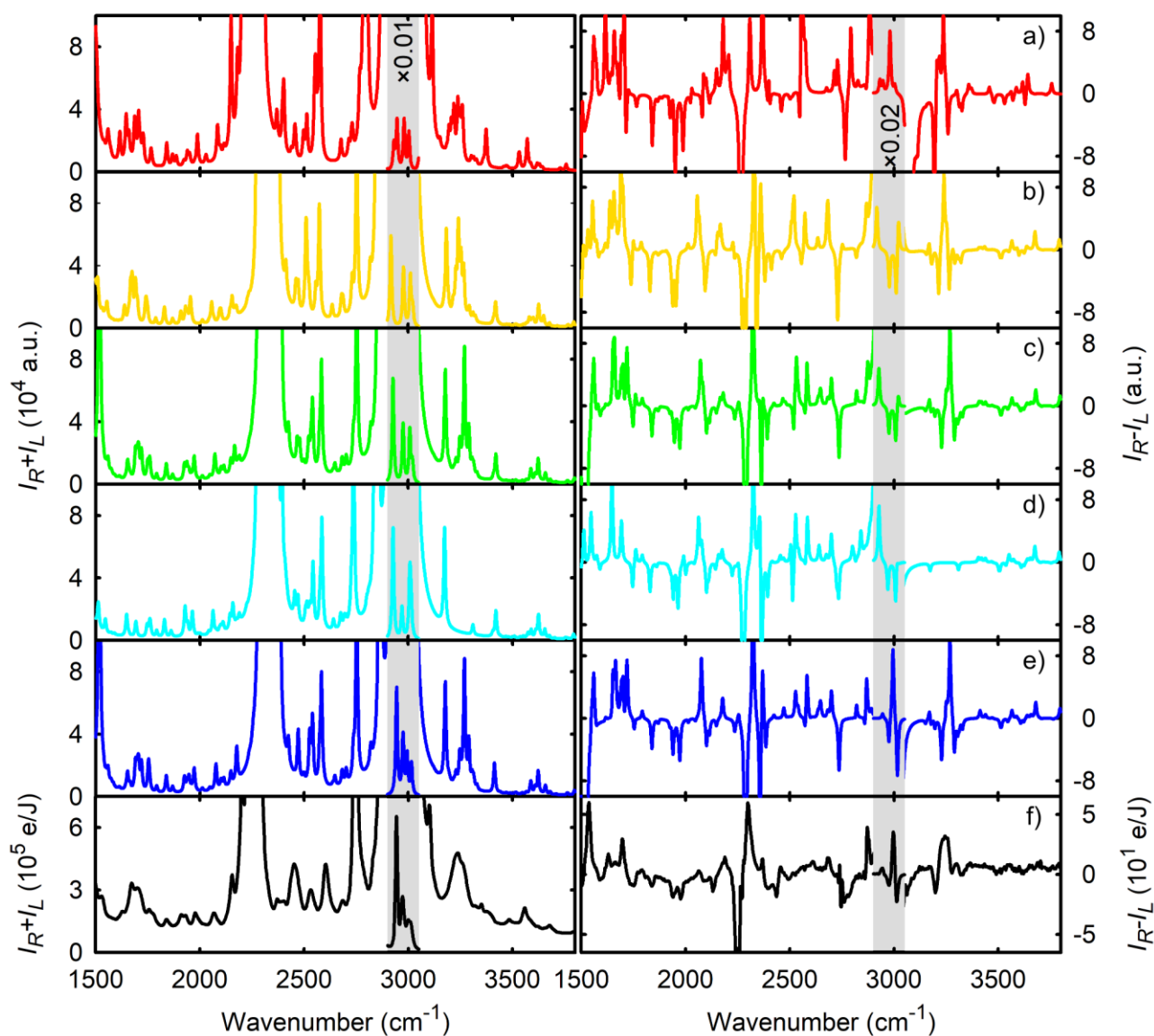


Figure S5. Nitrile Raman and ROA spectra within 1490-3800 cm^{-1} calculated using different methods: 6311G basis set (a), 6-311G** basis set (b), 6-311++G** basis set (c-e), all mode calculations (a-c, e) and with modes 1-4 frozen (d), and the GVPT2 (a-d) and VPT2 (e) approaches, (f) is the experiment.

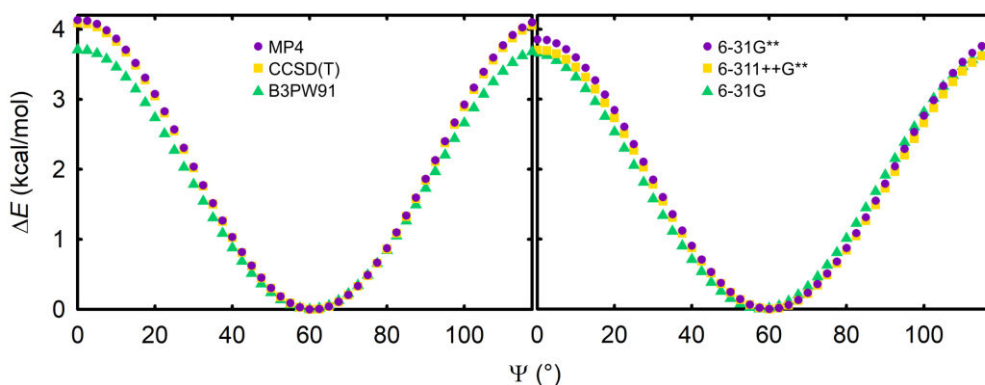


Figure S6. Calculated nitrile energy dependence on the Ψ angle (cf. **Figure 1**), calculated at different levels, left: MP4, CCSD(T) and B3PW91 with 6-311++G**/ (ACN), right: B3PW91 calculation in three basis sets.

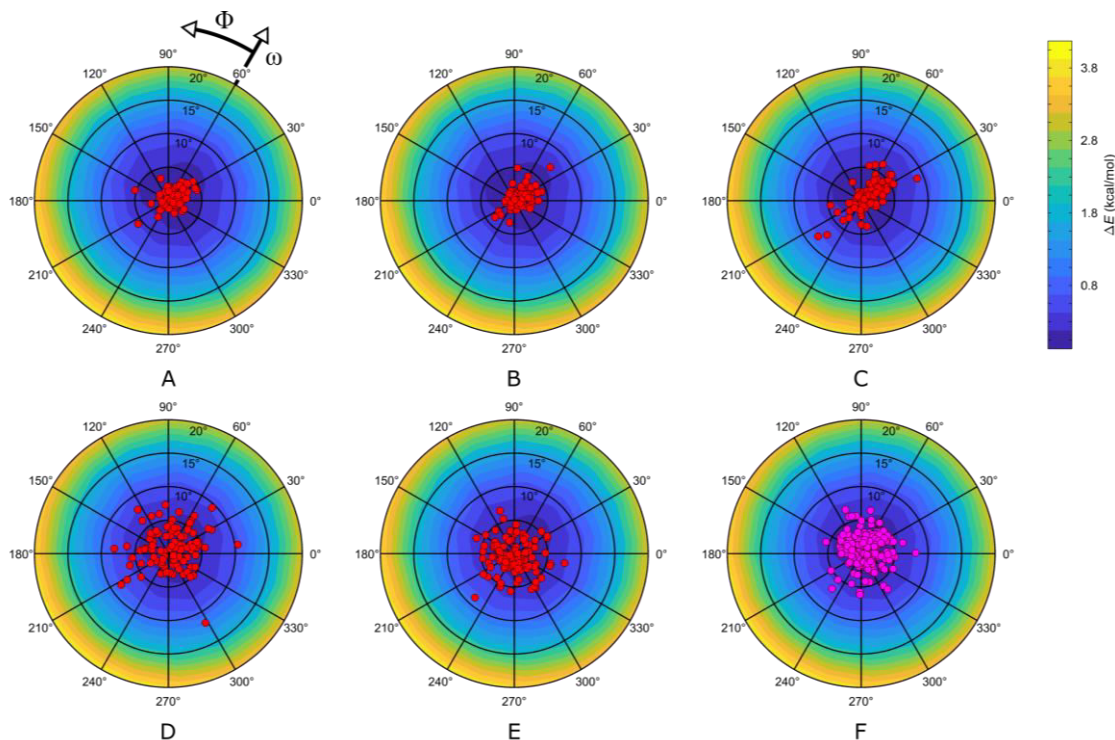


Figure S7. DFT energy as a function of the Φ and $180^\circ - \omega$ angles, and distributions of nitrile geometries in 200 clusters obtained from MD partially optimized with various values of the normal mode frequency limit (A: 40 cm^{-1} , B: 150 cm^{-1} , C: 225 cm^{-1} , D: 390 cm^{-1} , E: no optimization, F: exponential distribution within $50\text{-}900 \text{ cm}^{-1}$, see **Figure S2**).

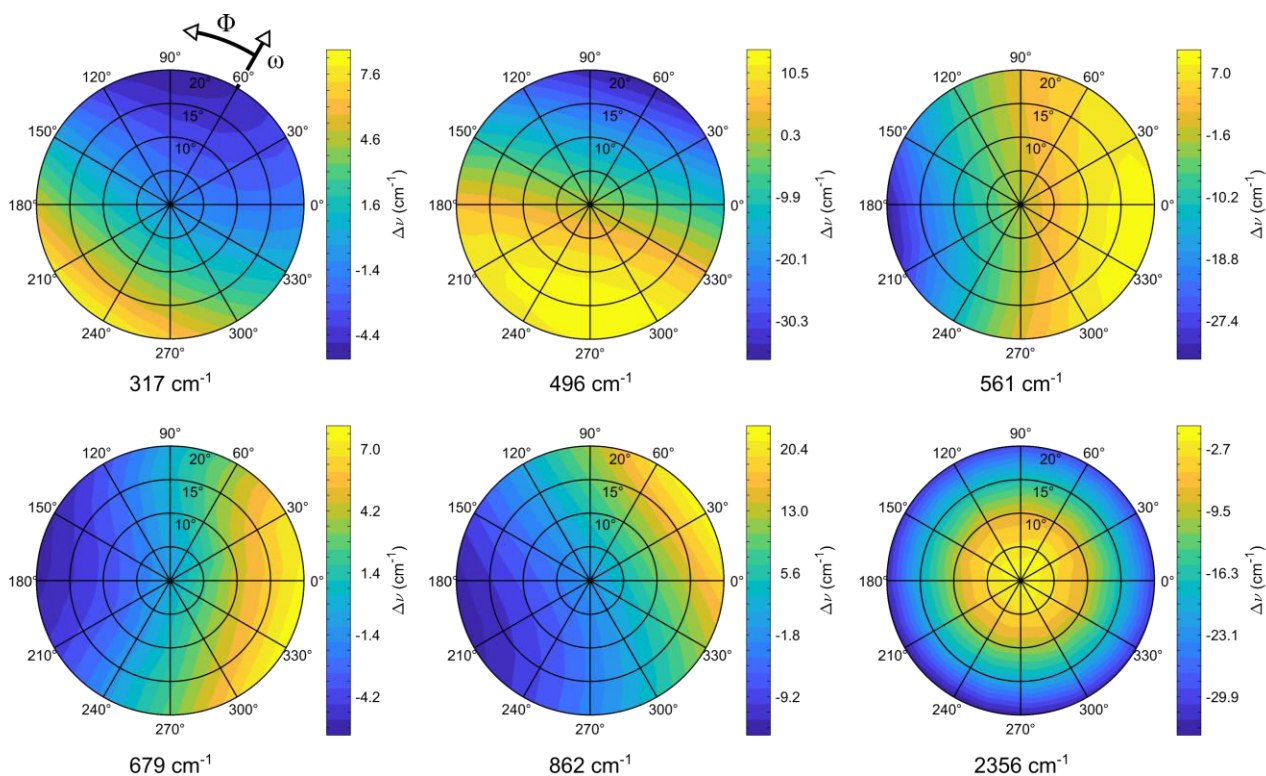


Figure S8. Frequency shift (Δ/cm^{-1}) of selected nitrile normal modes, from values for the equilibrium geometry, plotted as a function of the Φ and $180^\circ - \omega$ angles.

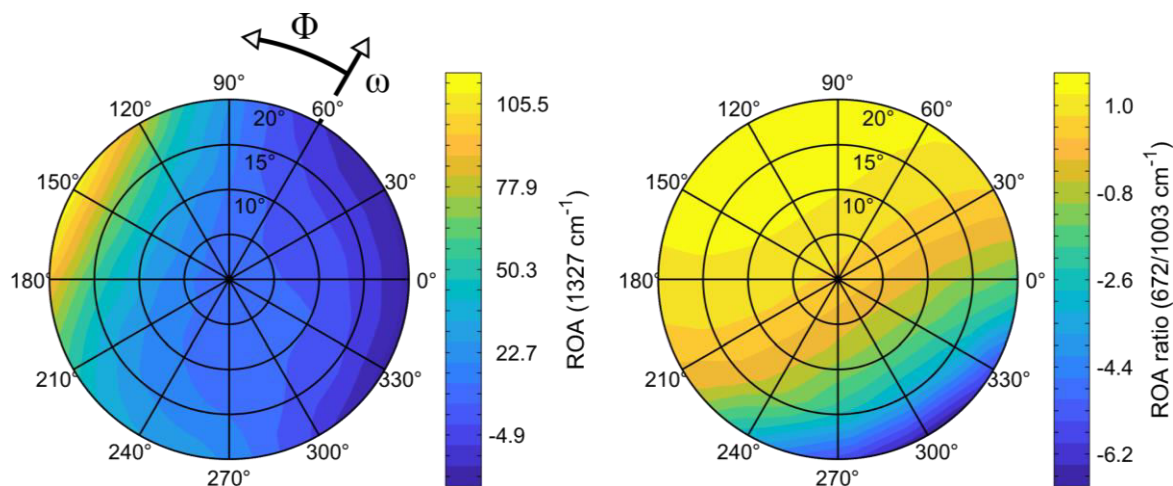


Figure S9. ROA intensity of the 1327 cm^{-1} nitrile mode (left), and intensity ratio of the 672 and 1003 cm^{-1} modes as dependent on the Φ and $180^\circ - \omega$ angles.

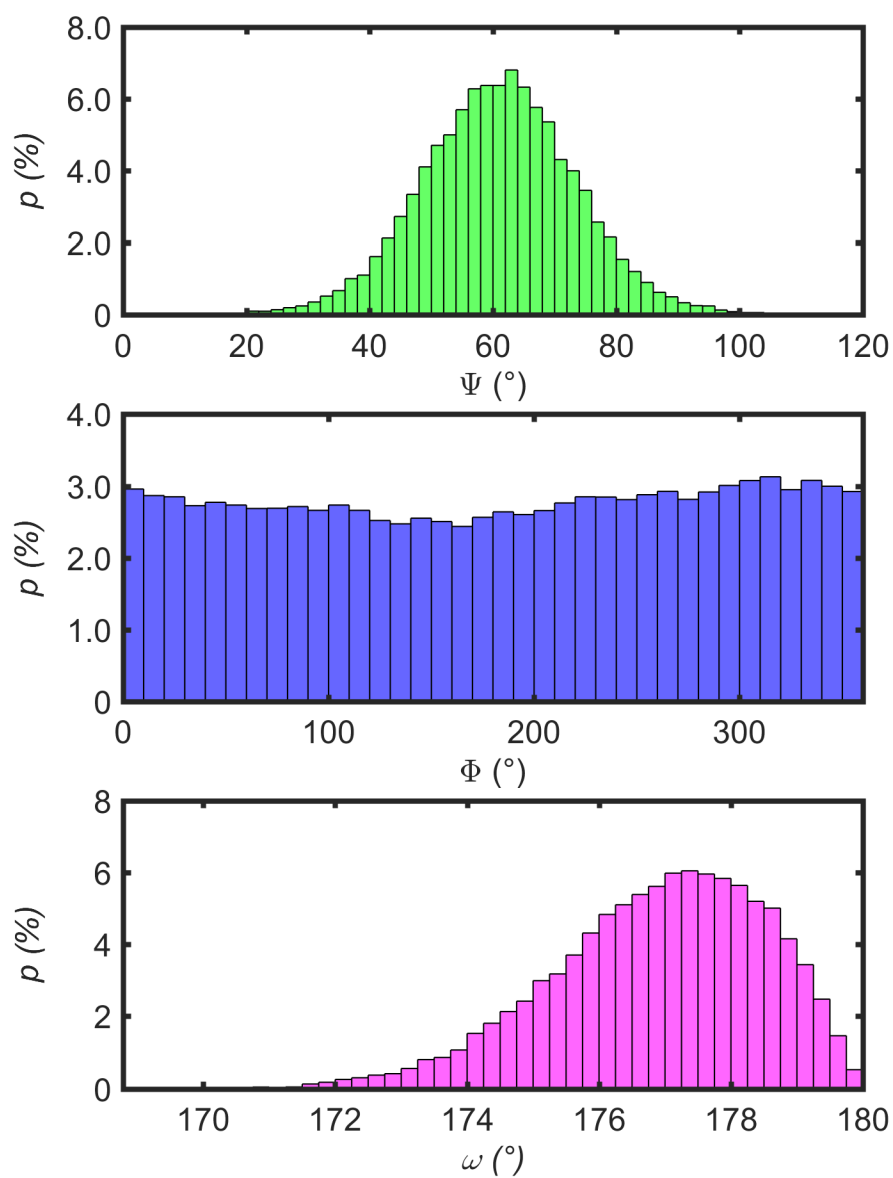


Figure S10. Angle distributions of the nitrile characteristic angles obtained during the free molecular dynamics run (1 ns).

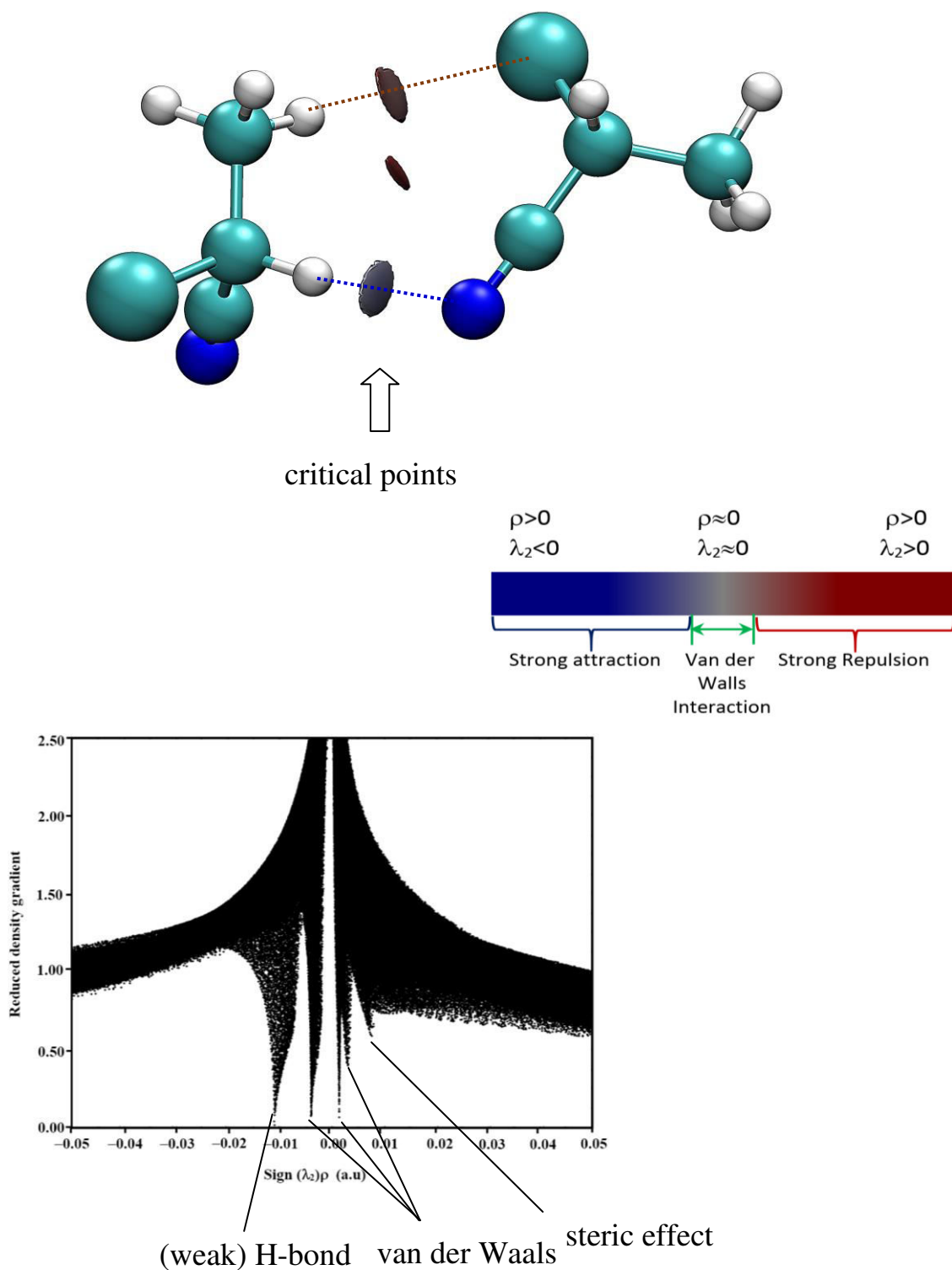


Figure S11. Example of the AIM analysis of nitrile-nitrile interactions (dimer number 9 in **Table S4**). Top – reduced density gradient (RDG) in critical points, bottom – RDG vs. signed density AIM graph.

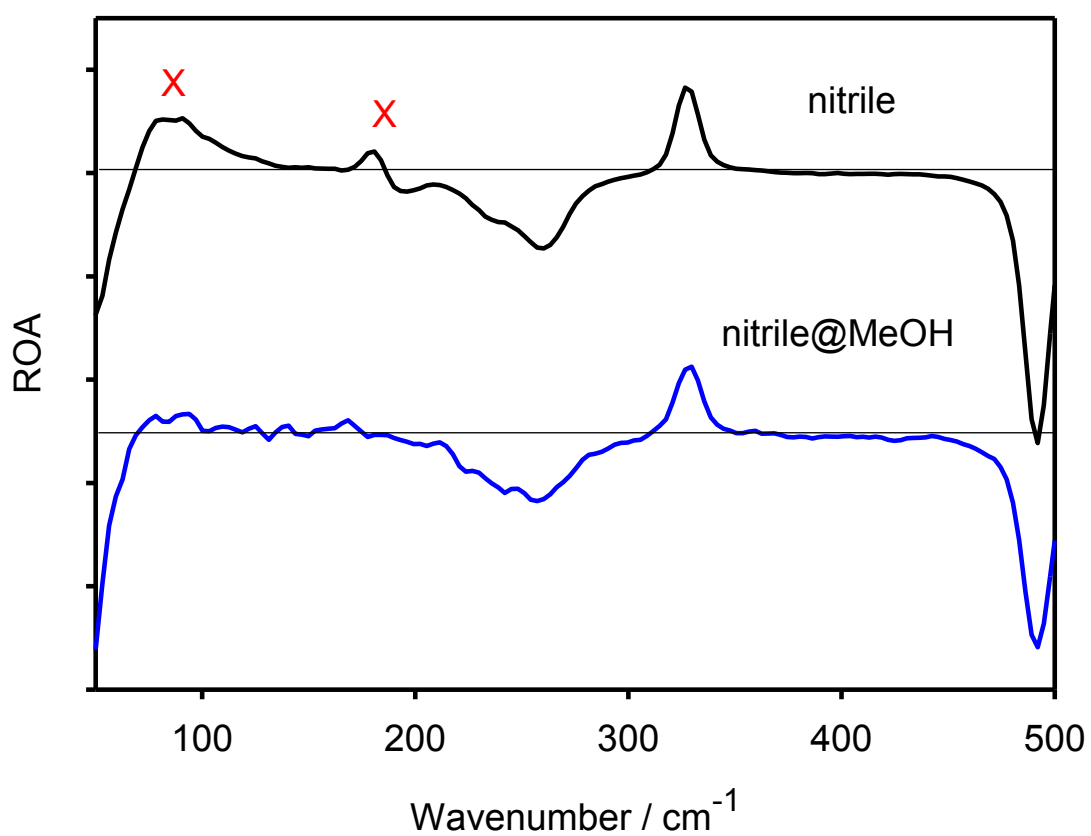


Figure S12. Nitrite ROA spectra in the low-frequency region, for pure liquid (top) and its about 10 % solution in methanol (bottom). Clearly vanishing bands are marked by the red crosses.

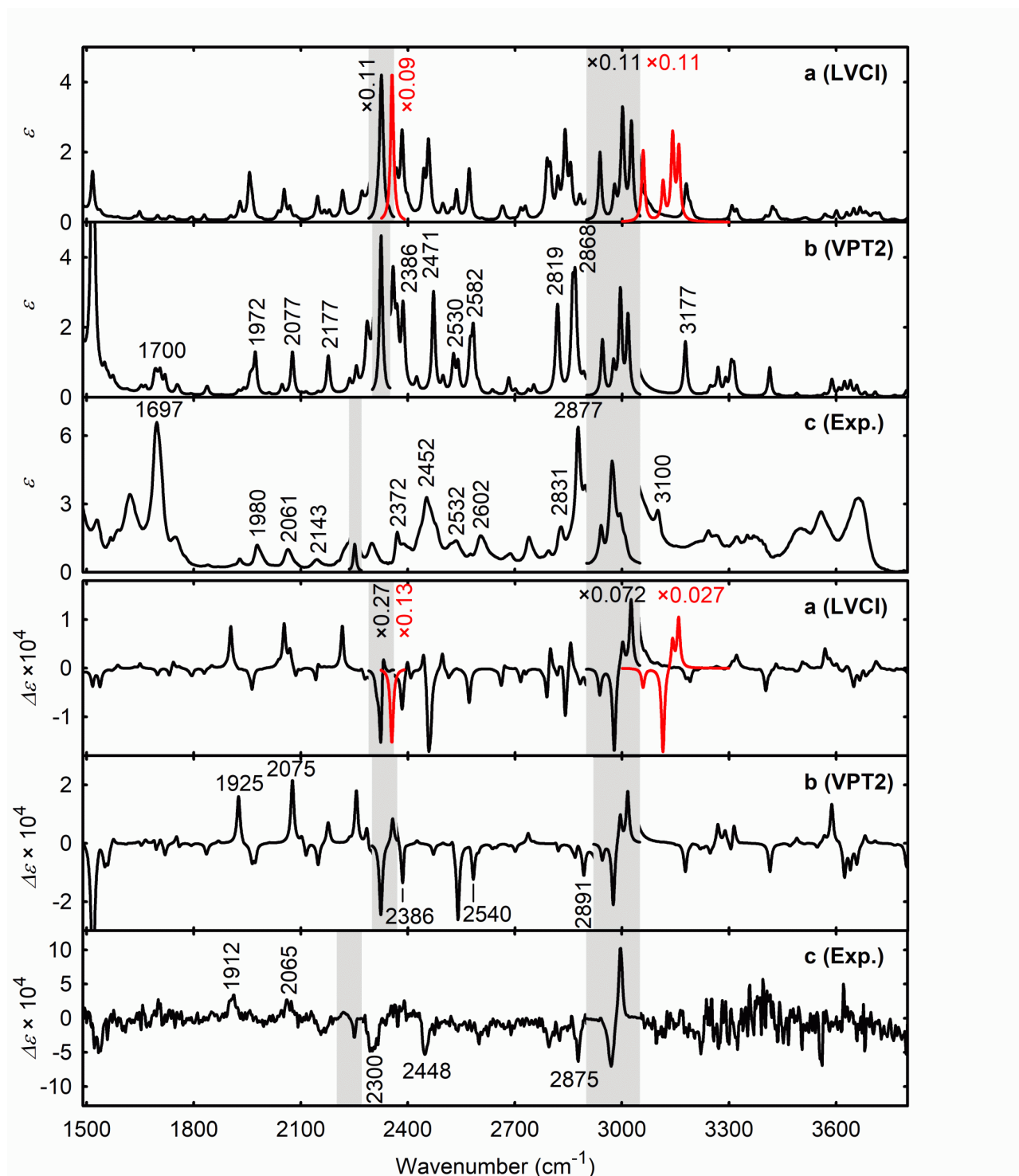


Figure S13. Nitrile IR and VCD spectra within 1490-3800 cm^{-1} calculated using the limited vibrational configuration interaction (a) and vibrational second order perturbation (b) methods, and experiment (c). For the C \equiv N and CH stretching spectra calculated at the harmonic level are plotted by the red line. The ϵ and $\Delta\epsilon$ units are $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.

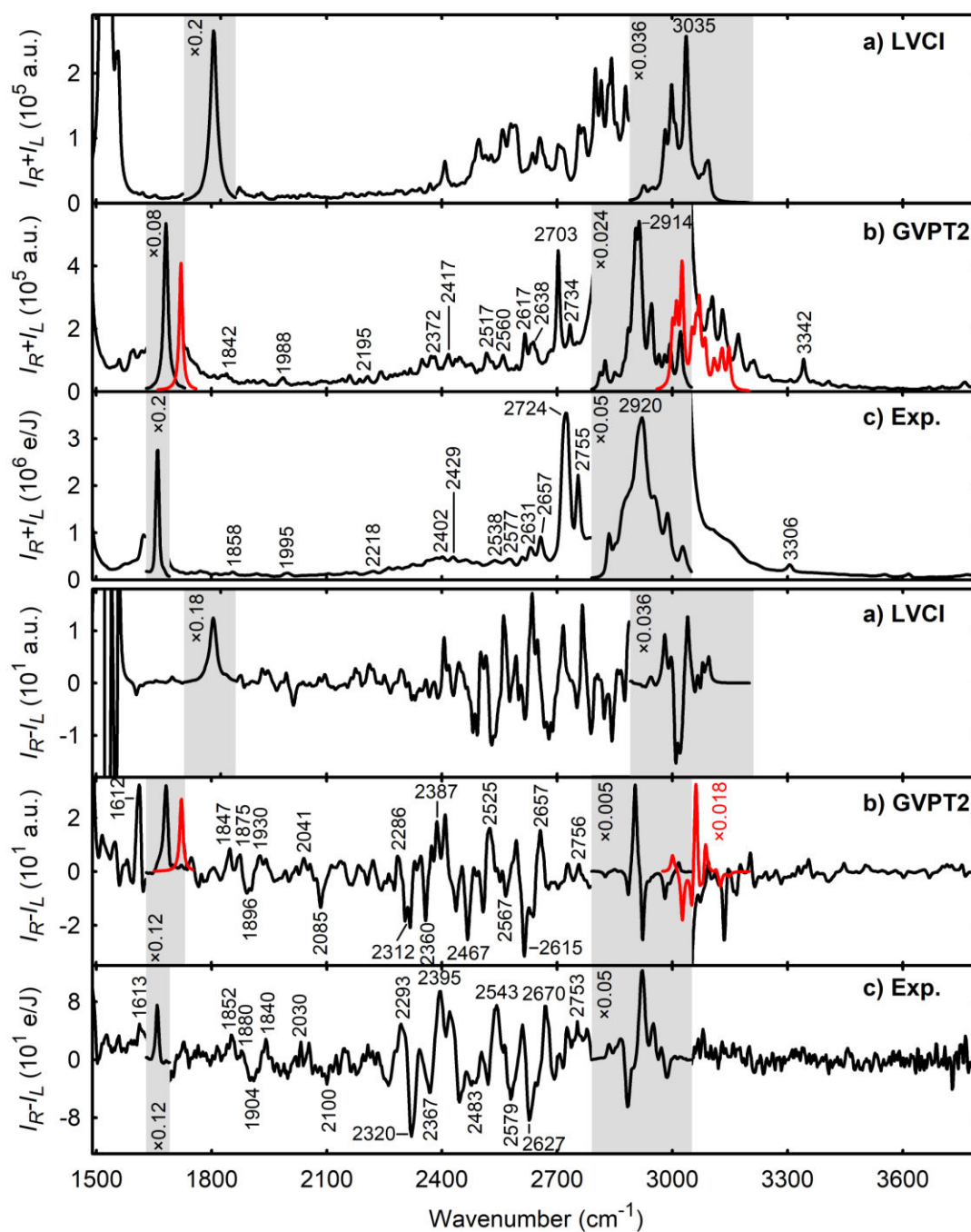


Figure S14. Raman and ROA spectra of α -pinene, plotted within 1490–3800 cm^{-1} , as calculated using the limited vibrational configuration interaction (a), generalized vibrational second order perturbation calculus (b), and the experiment (c). For the fundamental C \equiv N and CH stretching signal, spectral shapes calculated at the harmonic level are plotted by the red line. These signals in the gray areas are plotted in a different scale. LVCI spectra above 3100 cm^{-1} were not calculated.

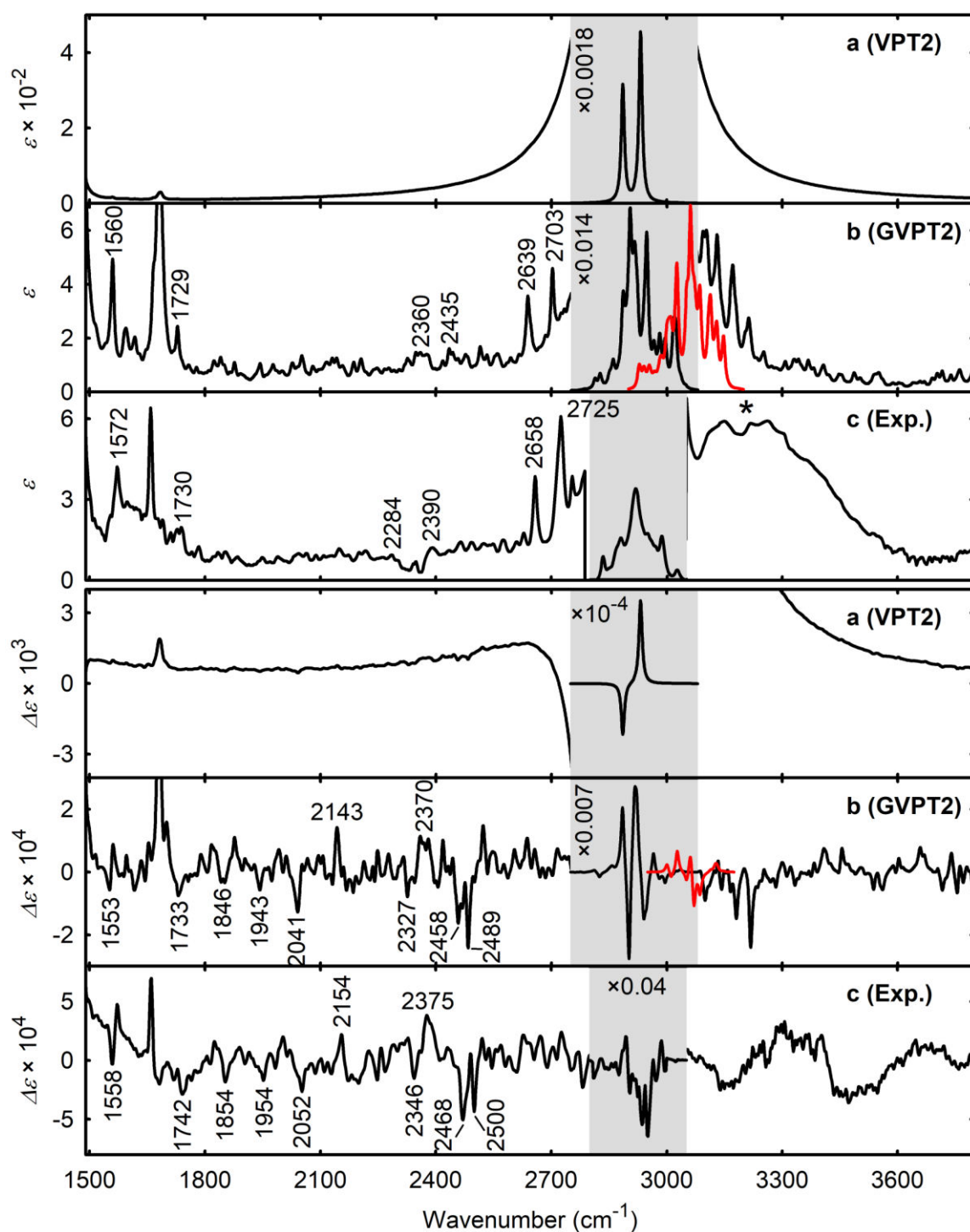


Figure S15. (+)- α -pinene IR and VCD spectra within 1490-3800 cm^{-1} calculated using vibrational second order perturbation before (a) and after including corrections to resonances (b), and experiment (c). For the CH stretching spectra calculated at the harmonic level are plotted by the red line. The ϵ and $\Delta\epsilon$ units are $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. Above 3100 cm^{-1} the experimental spectrum is hampered by BaF_2 absorption (marked by the asterisk, *), impossible to subtract.

Table S1. Laser power on the sample (P) and total accumulation time (t) used for ROA measurement. Weak combination and overtone bands of the nitrile were measured using different conditions (P^* , t^*). Reported spectra are normalized to unit excitation energy obtained as a product of the power and acquisition time.

| solvent | enantiomer | P / mW | t / h | P^* / mW | t^* / h |
|-----------------------|------------|----------|---------|------------|-----------|
| 2-chloropropionitrile | <i>R</i> | 83 | 9.7 | 340 | 29.7 |
| | <i>S</i> | 83 | 13.2 | 340 | 55.2 |
| α -pinene | <i>R</i> | 102 | 4.1 | - | - |
| | <i>S</i> | 68 | 9.8 | - | - |

Table S2. Nitrile, assignment of fundamental modes, frequencies in cm^{-1} .

| Mode | Harmonic | Anharmonic (VPT2) | EXP | Type |
|------|----------|----------------------|------|--|
| 1 | 3159 | 3016 | 3013 | asymmetric CH_3 stretching |
| 2 | 3142 | 2995 | 2997 | asymmetric CH_3 stretching |
| 3 | 3115 | 2971 | 2976 | αCH stretching |
| 4 | 3059 | 2945 | 2943 | symmetric CH_3 stretching |
| 5 | 2356 | 2325 | 2252 | CN stretching |
| 6 | 1476 | 1438 | 1456 | CH_3 scissoring |
| 7 | 1469 | 1439 | 1445 | CH_3 scissoring |
| 8 | 1403 | 1384 | 1383 | CH_3 umbrella motion |
| 9 | 1329 | 1300 | 1307 | CH bending |
| 10 | 1254 | 1264 | 1232 | CH bending |
| 11 | 1112 | 1104 | 1100 | CC stretching |
| 12 | 1091 | 1090 | 1077 | CC stretching |
| 13 | 1003 | 989 | 991 | CC stretching |
| 14 | 862 | 853 | 851 | CH_3 wagging, CCN bending |
| 15 | 679 | 664 | 681 | CH_3 wagging, CCN bending, CCl stretching |
| 16 | 561 | 571 | 547 | CCN bending to CH_3 |
| 17 | 496 | 494 | 489 | CCN bending perpendicular to CH_3 |
| 18 | 317 | 313 | 324 | CCCl bending, CCCN torsional twisting |
| 19 | 266 | 273 | 250 | CH_3 rotation |
| 20 | 227 | 252 | 231 | CH_3 rotation and, CCCN torsional twisting |
| 21 | 173 | 176 | 181 | CCN bending to CH_3 , CH_3 rocking |

Table S3. Nitrile, frequencies (cm^{-1}) of combination modes and overtones.

| Modes | Calculated (VPT2) | Experimental (Raman) |
|---|----------------------|-------------------------|
| 21+8; 20+9; 16+13 | 1560 | 1530 |
| 16+11; 15+13; 16+12 | 1653 | 1630 |
| 20+6; 20+7; 18+8; 2x14; 19+6; 19+7 | 1704 | 1674; 1700 |
| 18+6; 18+7; 15+11; 15+12; 17+10 | 1754 | 1757 |
| 16+10; 14+13 | 1839 | 1840 |
| 15+10; 17+6; 17+7; 14+11; 14+12; 16+8; 15+9 | 1925; 1945 | 1912; 1931 |
| 2x13 | 1973 | 1978 |
| 13+11; 13+12 | 2077 | 2068 |
| 2x11; 2x12; 11+12 | 2177 | 2155 |
| 13+6; 13+7 | 2424 | 2385 |
| 11+8; 12+8 | 2472 | 2453 |
| 12+6; 11+6; 11+7; 12+7; 2x10 | 2527; 2540 | 2532 |
| 10+9; 20+5; 19+5; 2x9 | 2583 | 2603 |
| 10+8; 9+8; 10+6; 10+7 | 2648; 2682; 2702 | 2685 |
| 2x8 | 2753 | 2745 |
| 8+6; 8+7 | 2820 | 2830 |
| 2x7; 2x6 | 2865 | 2877 |
| 21+2; 14+5; 21+1; 20+4 | 3177 | 3100 |
| 19+4; 19+3; 19+2; 19+1; 20+3; 20+2; 20+1; 18+4; 18+3; 18+2; 18+1; 13+5 | 3269 | 3238 |
| 11+5; 12+5 | 3413 | 3351 |
| 9+5 | 3623 | 3358 |

Table S4. AIM topological parameters of interacting atoms in 14 nitrile dimers. The inter-molecular threshold was 0.01 kcal/mol, electron density (ρ) and Laplacian ($\Delta\rho$) are in atomic units.

| Dimer number | Critical points ($\nabla\rho = 0$) | | | |
|--------------|--------------------------------------|--------------|----------------------|----------------------|
| | Atoms | Distance (Å) | ρ | $\Delta\rho$ |
| 1 | C-Cl | 1.8324 | 0.1653 | -0.185 |
| | C-N | 1.1526 | 0.4792 | 0.301 |
| | C-C | 1.4908 | 0.2559 | -0.648 |
| | C-H | 1.0900 | 0.4792 | -1.000 |
| 1 | C5...H17 | 4.7417 | 1.76×10^{-4} | 7.57×10^{-4} |
| | Cl9...H18 | 4.8686 | 1.67×10^{-4} | 6.54×10^{-4} |
| | Cl9...H11 | 4.6185 | 1.91×10^{-4} | 7.01×10^{-4} |
| | Cl14...H2 | 2.8821 | 6.00×10^{-3} | 2.10×10^{-2} |
| 2 | H16...N4 | 3.3554 | 1.72×10^{-3} | 5.76×10^{-3} |
| | H8...Cl14 | 2.9977 | 5.21×10^{-3} | 1.77×10^{-2} |
| 3 | H7...H16 | 2.7502 | 2.30×10^{-3} | 7.87×10^{-3} |
| | H18...Cl9 | 3.3750 | 2.14×10^{-3} | 7.67×10^{-3} |
| 4 | Cl14...Cl9 | 4.1806 | 2.26×10^{-3} | 6.29×10^{-3} |
| 5 | Cl9...Cl14 | 4.1894 | 1.83×10^{-3} | 5.39×10^{-3} |
| 6 | N15...N4 | 4.8218 | 2.42×10^{-4} | 9.67×10^{-4} |
| 7 | C5...Cl14 | 4.0798 | 2.06×10^{-3} | 6.25×10^{-3} |
| | H2...Cl14 | 3.5624 | 1.74×10^{-3} | 5.66×10^{-3} |
| 8 | N4...C12 | 3.2145 | 5.79×10^{-3} | 1.88×10^{-2} |
| | H11...N4 | 2.3913 | 1.08×10^{-2} | 3.40×10^{-2} |
| 9 | H16...Cl9 | 3.1998 | 3.90×10^{-3} | 1.29×10^{-2} |
| | H18...N4 | 3.7215 | 7.83×10^{-4} | 2.77×10^{-3} |
| 10 | N4...Cl14 | 4.6051 | 6.82×10^{-4} | 2.31×10^{-3} |
| 11 | Cl9...N15 | 4.4090 | 8.43×10^{-4} | 2.87×10^{-3} |
| 12 | Cl9...N15 | 4.9235 | 3.43×10^{-4} | 1.24×10^{-3} |
| | H6...H16 | 3.0306 | 1.32×10^{-3} | 4.43×10^{-3} |
| 13 | H7...Cl14 | 3.0265 | 4.95×10^{-3} | 1.65×10^{-2} |
| | N4...N15 | 3.5535 | 4.14×10^{-3} | 1.27×10^{-2} |
| 14 | N15...Cl9 | 3.5070 | 5.25×10^{-3} | 1.61×10^{-2} |
| | H6...Cl14 | 2.6718 | 1.02×10^{-2} | 3.54×10^{-2} |
| | Cl9...Cl14 | 4.0496 | 3.05×10^{-3} | 8.88×10^{-3} |