

Electronic supplementary information (ESI)

The keto/enol tautomerism in acetoacetyl fluoride: properties, spectroscopy, and gas-phase and crystal structures of the enol form

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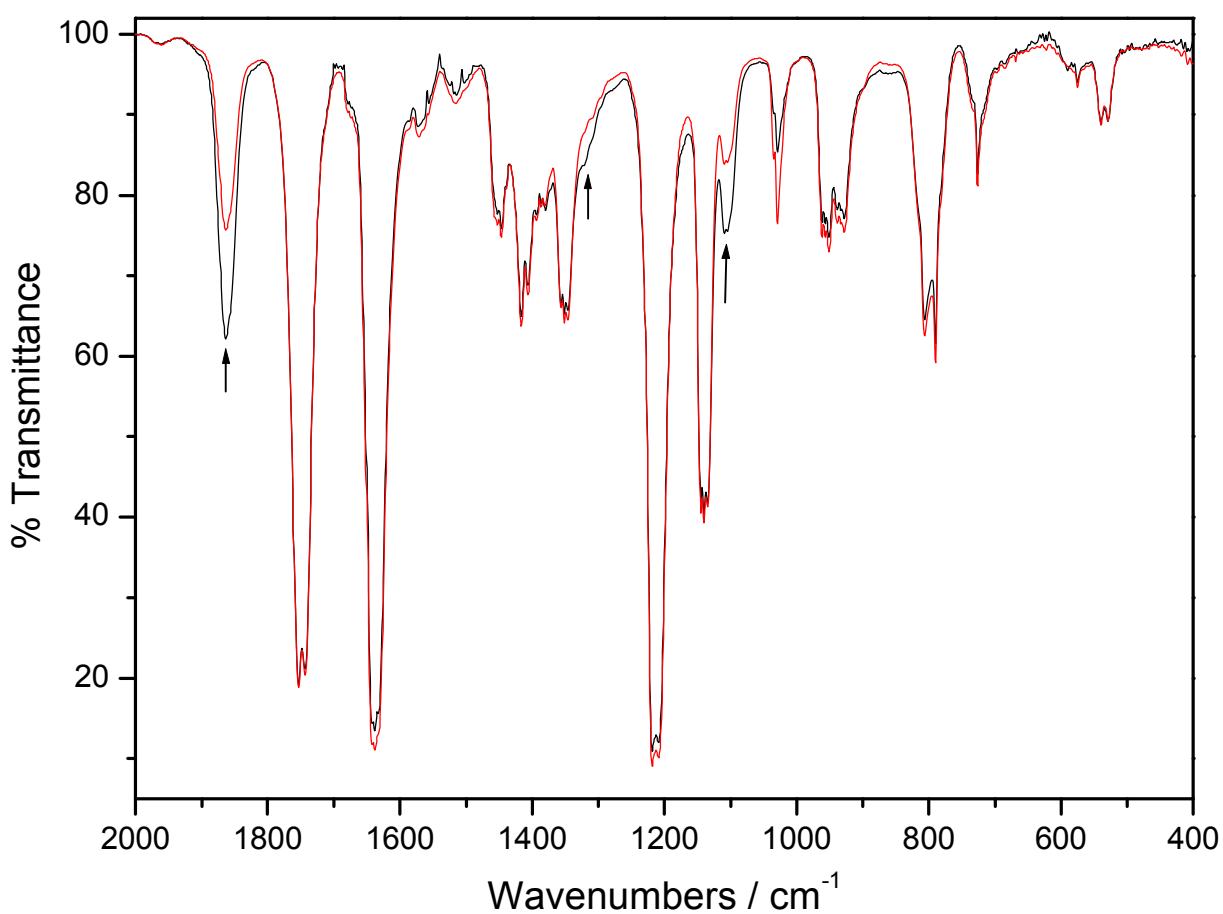


Figure S1. IR spectra of acetoacetyl fluoride as a mixture of both diketo and enol forms in the gas phase. Black line: spectrum recorded immediate after warming the liquid to gas. Red line: spectrum recorded after 5 min. Bands with apparent decreasing intensities are marked with upward arrowhead and attributed to the diketo form.

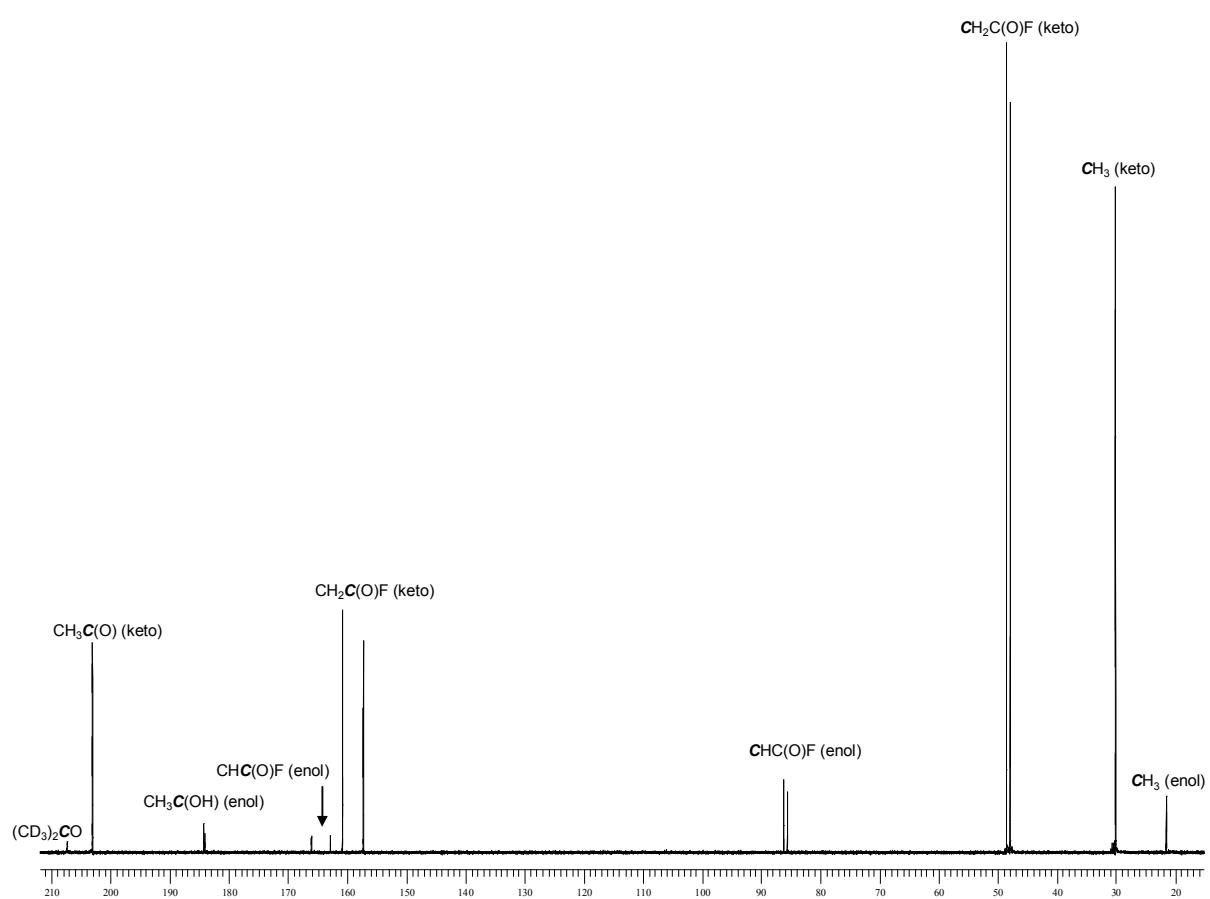


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of neat liquid acetoacetyl fluoride obtained at $-20\text{ }^\circ\text{C}$.

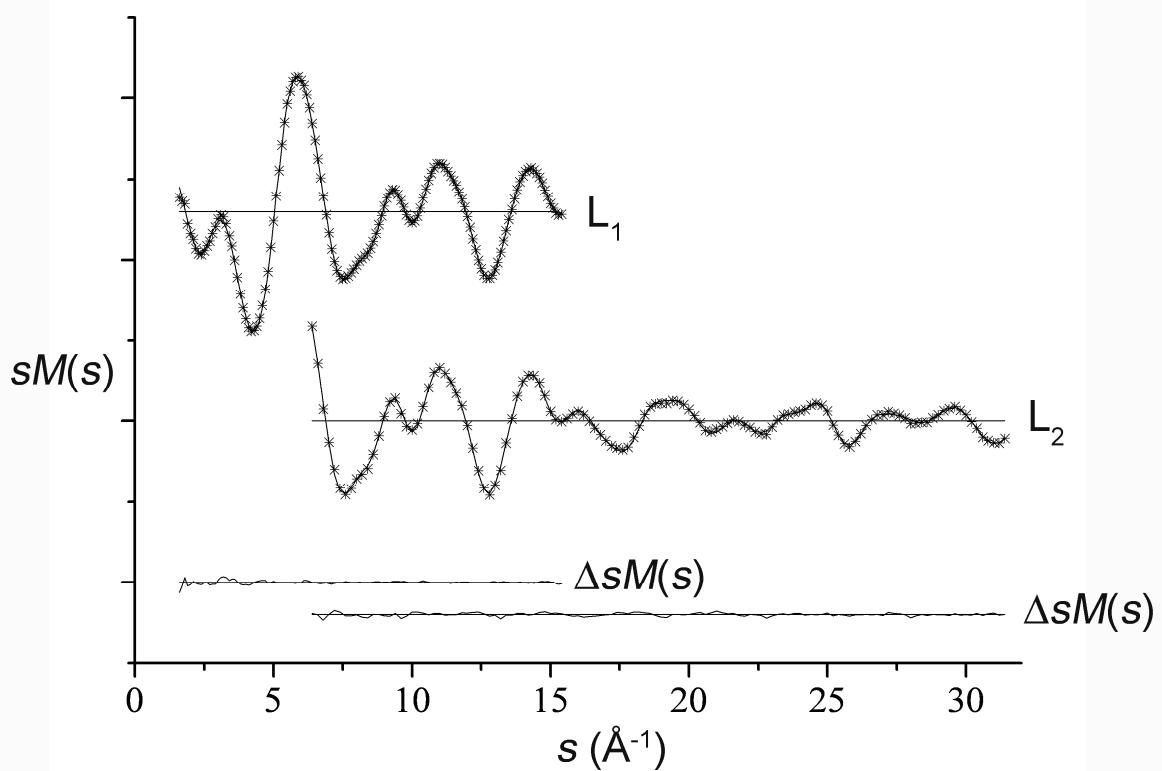


Figure S3. Experimental (dots) and calculated (solid lines) modified molecular intensity curves and residuals (experimental-theoretical) at two nozzle-to-plate distances ($L_1 = 500$ mm, $L_2 = 250$ mm).

Table S1. Interatomic distances, experimental (l (GED)) and calculated l (B3LYP/cc-pVTZ) vibrational amplitudes and vibrational corrections ($r_{h1}-r_a$) for the enol tautomer (excluding nonbonded distances involving hydrogen).^a

| | r_{h1} | l (GED) | l (B3LYP/cc-pVTZ) | $r_{h1}-r_a$ |
|---------|-----------|---------------------------------|---------------------|--------------|
| O2-H1 | 0.982(6) | 0.078(6) <i>l1</i> ^b | 0.074 | 0.0012 |
| C2-H2 | 1.071(6) | 0.079(6) <i>l1</i> | 0.075 | 0.0019 |
| C4-H3 | 1.081(6) | 0.081(6) <i>l1</i> | 0.076 | 0.0016 |
| C4-H4 | 1.086(6) | 0.082(6) <i>l1</i> | 0.077 | 0.0017 |
| C4-H5 | 1.086(6) | 0.082(6) <i>l1</i> | 0.077 | 0.0017 |
| C1-O1 | 1.208(5) | 0.045(5) <i>l2</i> | 0.038 | 0.0002 |
| C3-O2 | 1.335(8) | 0.050(5) <i>l2</i> | 0.044 | 0.0003 |
| C1-F | 1.347(5) | 0.053(5) <i>l2</i> | 0.046 | 0.0008 |
| C2-C3 | 1.369(4) | 0.050(5) <i>l2</i> | 0.043 | 0.0006 |
| C1-C2 | 1.436(4) | 0.054(5) <i>l2</i> | 0.047 | 0.0010 |
| C3-C4 | 1.495(4) | 0.056(5) <i>l2</i> | 0.049 | 0.0004 |
| O1···F | 2.207(5) | 0.051(2) <i>l3</i> | 0.052 | 0.0037 |
| C2···F | 2.339(7) | 0.059(2) <i>l3</i> | 0.060 | 0.0027 |
| O2···C4 | 2.391(10) | 0.062(2) <i>l3</i> | 0.063 | 0.0047 |
| C2···O2 | 2.361(9) | 0.053(2) <i>l3</i> | 0.054 | 0.0022 |
| C2···O1 | 2.361(8) | 0.053(2) <i>l3</i> | 0.054 | 0.0026 |
| C1···C3 | 2.436(7) | 0.055(2) <i>l3</i> | 0.056 | 0.0035 |
| C2···C4 | 2.522(8) | 0.062(2) <i>l3</i> | 0.063 | 0.0024 |
| O1···O2 | 2.623(10) | 0.105(2) <i>l3</i> | 0.106 | -0.0035 |
| C1···O2 | 2.799(9) | 0.084(5) <i>l4</i> | 0.078 | 0.0025 |
| C3···O1 | 2.853(10) | 0.084(5) <i>l4</i> | 0.078 | 0.0017 |
| C3···F | 3.607(9) | 0.067(7) <i>l5</i> | 0.060 | 0.0106 |
| C1···C4 | 3.835(10) | 0.072(7) <i>l5</i> | 0.065 | 0.0087 |
| O2···F | 4.137(10) | 0.077(8) <i>l6</i> | 0.079 | 0.0118 |
| O1···C4 | 4.348(11) | 0.081(8) <i>l6</i> | 0.083 | 0.0082 |
| C4···F | 4.860(12) | 0.092(10) <i>l7</i> | 0.078 | 0.0174 |

^a Values in Å. Error limits for the amplitudes are 3σ values. For atom numbering see Figure 1.

^b Group number of amplitude

Table S2. Conditions of GED experiment

| | | |
|------------------------------|--------------------|--------------------|
| Nozzle-to-plate distance, mm | 500 | 250 |
| Electron beam, nA | 230 | 180 |
| Electron wavelength , Å | 0.04830(1) | 0.04839(1) |
| Exposure time, s | 30-61 | 60-61 |
| Residual gas pressure, mbar | 8×10^{-6} | 7×10^{-6} |