Coherence in Nonradiative Transition: Internal Conversion in Rydberg-Excited N-Methyl and N-Ethyl Morpholine

Yao Zhang¹, Hannes Jónsson¹,², Peter M. Weber¹

¹ Department of Chemistry, Brown University, Providence, RI 02912, USA.
² Faculty of Physical Sciences, University of Iceland, 107 Reykjavík, Iceland.

Supporting information

1. The time-resolved photoelectron spectra of NMM at various excitation wavelengths.

2. Time constants for dynamic processes.

3. List of harmonic vibrational frequencies of NMM and NEM at the ion state geometry calculated with B3LYP/6-311++G(d,p) method.
1. The time-resolved photoelectron spectra of NMM at various excitation wavelengths.

Figure SI1: The time-resolved photoelectron spectra of NMM (top row, left) excited at 194 nm, probed at 270 nm; (middle) excited at 208 nm, probed at 404 nm; (right) excited at 214 nm, probed at 403 nm; (bottom row, left) excited at 220 nm, probed at 404 nm; (middle) excited at 226 nm, probed at 404 nm; (right) excited at 230 nm, probed at 404 nm. (The spectrum with 226 nm excitation is from reference 1.)
2. Time constants for dynamic processes.

Table SI1. Fitted time constants of the dynamic processes, with the uncertainties (3σ) listed in parentheses, for the excitation wavelengths studied.

<table>
<thead>
<tr>
<th>Wavelength λ / nm</th>
<th>Internal conversion τc / fs (^1)</th>
<th>Oscillation period T / fs</th>
<th>Damping τd / fs</th>
<th>Phase ϕ / rad</th>
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<tr>
<td>230</td>
<td>--</td>
<td>648 (20)</td>
<td>646 (107)</td>
<td>0.57 (0.23)</td>
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<tr>
<td>226</td>
<td>--</td>
<td>650 (13)</td>
<td>750 (90)</td>
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<td>220</td>
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<td>651 (33)</td>
<td>648 (180)</td>
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<tr>
<td>214(^2)</td>
<td>120 (3)</td>
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<td>0.52 (0.69)</td>
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<td>208</td>
<td>106 (6)</td>
<td>630 (38)</td>
<td>520 (197)</td>
<td>2.47 (0.21)</td>
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<td>194(^3)</td>
<td>140 (30)</td>
<td>650</td>
<td>580</td>
<td>2.95 (0.44)</td>
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\(^1\) The parameter τc is obtained from the fit of the 3p time trace and then treated as a fixed parameter in the fit of the 3s time trace.

\(^2\) 214 nm is fitted differently, because both 3s and 3p are excited, so a linear combination of the two are fitted. To reduce the number of parameters to make the fit work, the period and damping are fixed at a nearby wavelengths' results. Only the phases (and some coefficients) are treated as variables.

\(^3\) 194 nm data was obtained using a 266 nm probe pulse.
3. List of harmonic vibrational frequencies of NMM and NEM at the ion state geometry calculated with B3LYP/6-311++G(d,p) method.

**NMM frequencies (cm$^{-1}$)**

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<thead>
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<th>Frequency</th>
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**NEM frequencies (cm$^{-1}$)**

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