CONCENTRATION DETERMINATIONS FOR REACTIVE CHEMICAL INTERMEDIATES USING EMPIRICALLY DETERMINED AND THEORETICALLY CALCULATED TRANSITION PROBABILITIES

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Introduction

The Beer–Lambert law, after invoking several usually applicable approximations, shows that the fractional absorption of radiation on a transition between two quantum states is proportional to the concentration of molecules present in the lower state. For non-reactive molecules, a suitable standard of known concentration/pressure can be used to determine the proportionality constant, i.e., the product of the path length and molecular cross section. However, for many chemical intermediates such as free radicals, their reactivity precludes preparing such a standard of known concentration.

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Spectra simulation

Cross-sections and experimental measurements are related via the Beer–Lambert law:

\[ I = I_0 \exp(-\sigma N L) = I_0 (1 - \sigma N L) \]

where \( \sigma \) is the absorption cross section at a given wavelength, \( \Delta N \) is the difference in the number density between the upper and lower states, \( N \) is the number density of a measured state, and \( L \) is the path length of absorbing medium.

If there is a Boltzmann equilibrium, absolute populations of molecules in a given quantum state can be straightforwardly expressed in terms of the total species population \( N_v \). If \( N_v \) and \( L \) can be independently measured, the concentration can be readily determined from the experimentally measured fractional absorption \( a \).

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\[ \frac{I_0 - I}{I_0} = \sigma N L = a \]

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This empirical cross-section is related to fundamental molecular properties [3]. These relations are somewhat complicated, but modern spectral simulation programs like PGOPHER include them and can be used to simulate \( \sigma \) as a function of spectral wavelength. We have used PGOPHER to simulate the relevant CRDS peroxo radical spectra under the given experimental conditions, using molecular constants, i.e., rotational, spin–rotational, etc., obtained from experiment or determined by ab initio calculations. Examples of such simulations are compared with the observed spectra in Figs. 1 and 2. These simulations were adjusted to match the experimental cross sections by varying one PGOPHER input parameter, the vibronic transition dipole moment (VTDM), with the resulting values given in Table 2.

Ab initio calculation of vibronic transition dipole moment

One can also calculate the VTDMs, \( M_{\text{ vibronic}} \), using the relationship

\[ M_{\text{ vibronic}} = \frac{G_{\text{ vibronic}}}{\beta} M_{\text{ AX}} \]

where \( G_{\text{ vibronic}} \) is the Frank–Condon (FC) overlap integral, and \( M_{\text{ AX}} = \langle A | \mu | X \rangle \) is the electronic transition dipole moment (ETDM) for the experimentally observed \( A \rightarrow X \) electronic transition of the peroxyl radicals. To calculate the FC overlap integral, geometry optimization and normal mode analysis were performed for the ground and excited states using the UHF-CCSD(T)/ANO1 method. The FC overlap integral was obtained as the square root of the FC factor calculated with the “FC-squared” (FCF2) program available in CFOUR. The ETDM values for the \( A \rightarrow X \) transition were calculated at both the \( A \) and \( X \) state optimized geometries using the UHF-EOMEE-CCSD/aug-cc-pVTZ method. Averaging these ETDM values accounts for its linear dependence on geometry. Based on extensive calculations for HO₂, a scaling factor of 0.95 was adopted for all RO₂ radicals to account for higher-level electron correlation and basis set error effects on the ETDM with the results listed in Table 2.

Results

Fig. 1: Section [4] of rotationally resolved HO₂ spectrum (red) vs simulation of spectrum via PGOPHER (black).

Fig. 2: Methyl peroxyl radical \( A \rightarrow X \) experimental spectrum [5] (Black) vs PGOPHER simulation (Red).

Comparison

Table 1. Excitation energies, \( E_{\text{exc}} (A \rightarrow X) \) (cm⁻¹)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calculation</th>
<th>Experiment</th>
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<tbody>
<tr>
<td>HO₂</td>
<td>0.7375</td>
<td>0.03710</td>
</tr>
<tr>
<td>CH₂O₂</td>
<td>0.6137</td>
<td>0.03688</td>
</tr>
<tr>
<td>g(CH₂O₂)</td>
<td>0.6191</td>
<td>0.02995</td>
</tr>
<tr>
<td>f(CH₂O₂)</td>
<td>0.6820</td>
<td>0.08365</td>
</tr>
</tbody>
</table>

*Refers to the VTDMs listed in Table 2 are statistical only. They do not include systematic errors introduced in the measurement of \( N_v \) or \( L \), which may give errors up to 40% or greater.

Acknowledgements

References