

# 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 and accounts for the frequent absence of their cross sections in molecular line lists. Nonetheless, such molecules play important roles in chemical reactions of significance both economically and environmentally; hence spectroscopic measurements of their concentrations can be very valuable. Peroxy radicals, RO<sub>2</sub> (R = H or alkyl group), are important intermediates in combustion and tropospheric chemistry. Experimental cross-sections have been reported for several peroxy radicals that have been observed by cavity ringdown absorption spectroscopy (CRDS) using indirect means to determine their concentrations. Today it is also possible to calculate cross sections for individual rovibronic transitions using a combination of quantum chemistry methods and spectral simulation software. In our work the CFOUR [1] quantum chemistry suite and the PGOPHER [2] spectral simulation software are used. The purpose of this poster is to describe our computational approach and compare its results with experimentally determined values.

## Spectra simulation

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

$$I = I_0 \exp(-\sigma \Delta N L) \approx I_0(1 - \sigma \Delta N L) \quad \frac{I_0 - I}{I_0} = \sigma \Delta N L = \alpha$$

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  $N_T$ . If  $N_T$  and  $L$  can be independently measured, the concentration can be readily determined from the experimentally measured fractional absorption  $\alpha$ .

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 peroxy 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,  $M_{\text{vibr}}$ , using the relationship

$$M_{\text{vibr}} = G_{v''v'} M_e^{AX}$$

where  $G_{v''v'} = \langle v''(q'') | v'(q') \rangle$  is the Frank–Condon (FC) overlap integral, and  $M_e^{AX} = \langle \tilde{A} | \mu | \tilde{X} \rangle$  is the electronic transition dipole moment (ETDM) for the experimentally observed  $\tilde{A} \leftarrow \tilde{X}$  electronic transition of the peroxy 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” ([FC]<sup>2</sup>) program available in CFOUR. The ETDM values for the  $\tilde{A} \leftarrow \tilde{X}$  transition were calculated at both the  $\tilde{X}$  and  $\tilde{A}$  state optimized geometries using the UHF-EOMEE-CCSD/aug-pVTZ method. Averaging these ETDM values accounts for its linear dependence on geometry. Based on extensive calculations for HO<sub>2</sub>, a scaling factor of 0.95 was adopted for all RO<sub>2</sub> radicals to account for higher-level electron correlation and basis set error effects on the ETDM with the results listed in Table 2.

## Results

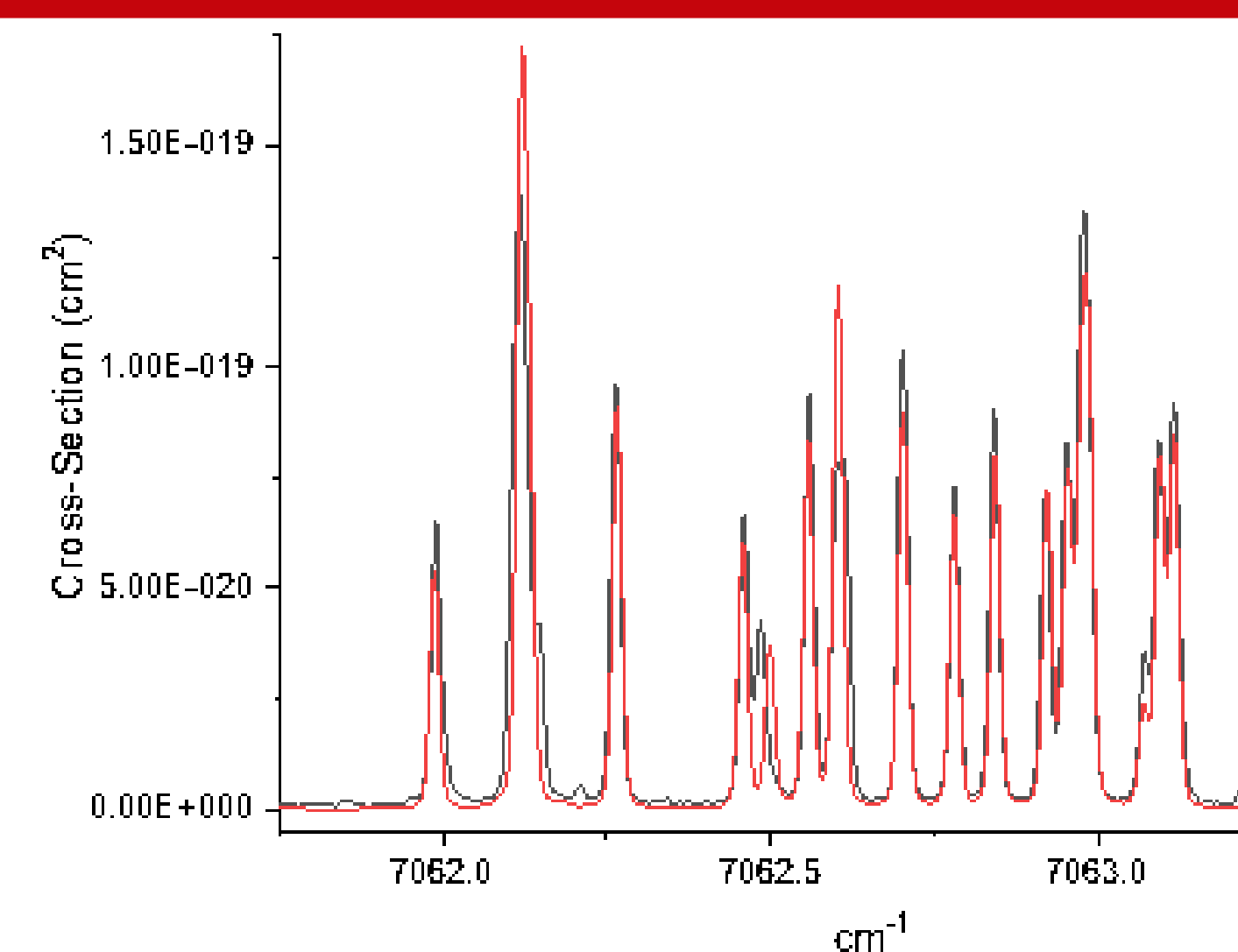


Fig. 1: Section [4] of rotationally resolved HO<sub>2</sub> spectrum (red) vs simulation of spectrum via PGOPHER (black)

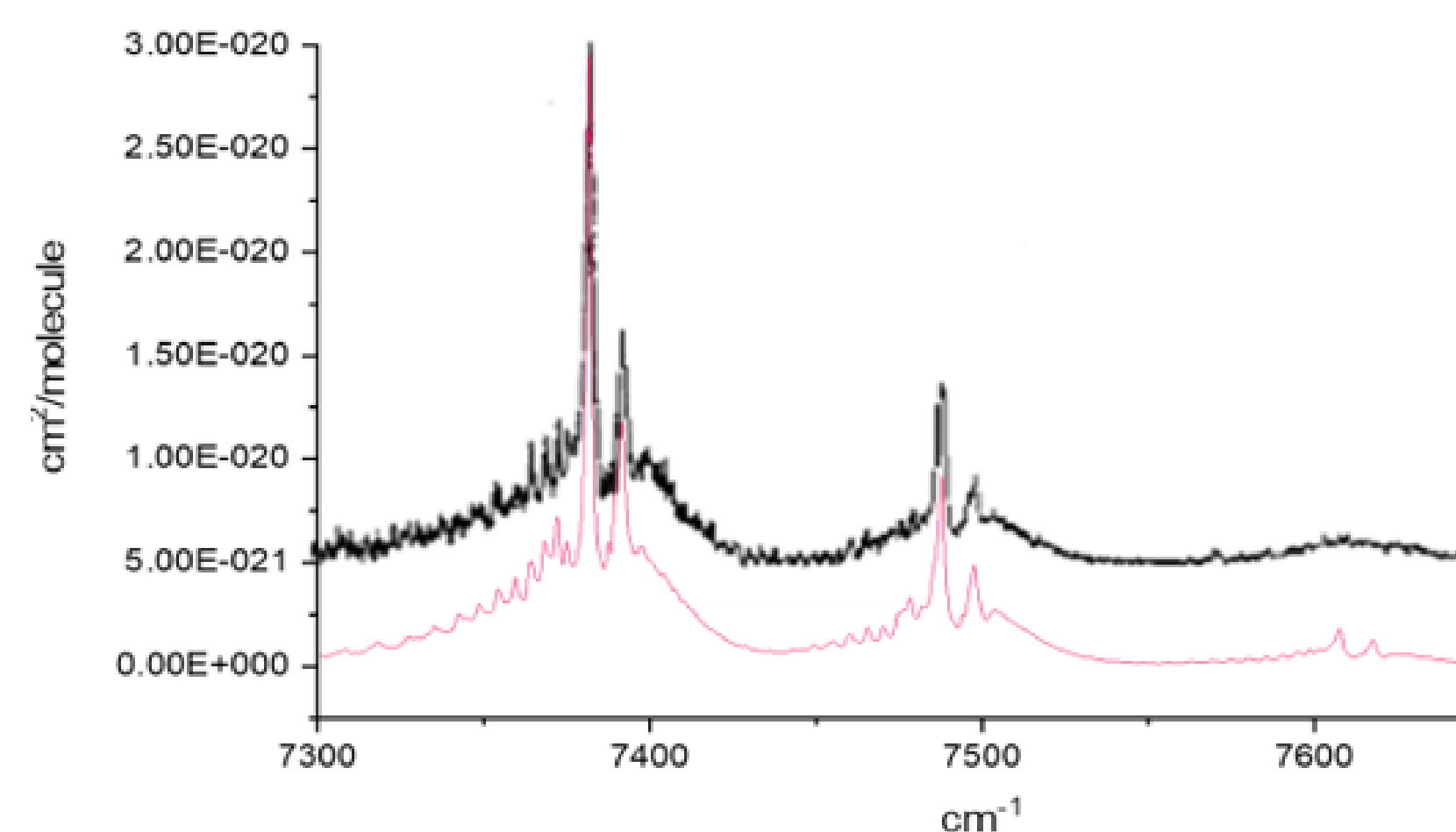


Fig. 2: Methyl peroxy radical  $\tilde{A} \leftarrow \tilde{X}$  experimental spectrum [5] (Black) vs PGOPHER simulation (Red)

## Comparison

Table 1. Excitation energies,  $T_{00}(\tilde{A} \leftarrow \tilde{X})$  (cm<sup>-1</sup>)

	Calc	Expt	Ref.
HO <sub>2</sub>	6844	7030	[4]
CH <sub>3</sub> O <sub>2</sub>	7128	7383	[5]
<i>g</i> -CH <sub>3</sub> CH <sub>2</sub> O <sub>2</sub>	7698	7593	[6, 7]
<i>t</i> -CH <sub>3</sub> C(O)O <sub>2</sub>	5554	5583	[8, 9]

To benchmark our ab initio calculations, we compare the adiabatic  $\tilde{A} \leftarrow \tilde{X}$  excitation energies calculated with ZPE corrections (shown in Table 1). The calculated excitation energies show good agreement with experiment. The largest deviation from experiment, 255 cm<sup>-1</sup> (3.5 %), is obtained for CH<sub>3</sub>O<sub>2</sub>.

Table 2. Franck–Condon factor overlaps,  $G_{v''v'}$ , electronic (ETDM) and vibronic transition dipole moments (VTDM) (Debye)

	Calculation			Experiment	
	$G_{v''v'}$	ETDM	VTDM	VTDM	Ref.
HO <sub>2</sub>	0.7375	0.03710	0.02736	0.02072(14)	[4]
CH <sub>3</sub> O <sub>2</sub>	0.6137	0.03688	0.02263	0.01711(150)	[5]
<i>g</i> -CH <sub>3</sub> CH <sub>2</sub> O <sub>2</sub>	0.6191	0.02995	0.01854	0.01560(240)	[6, 7]
<i>t</i> -CH <sub>3</sub> C(O)O <sub>2</sub>	0.6820	0.08365	0.05704	0.035 <sup>a</sup>	[8, 9]

<sup>a</sup> tentative

The errors for the VTDMs listed in Table 2 are statistical only. They do not include systematic errors introduced in the measurement of  $N_T$  or  $L$ , which may give errors up to 40 % or greater. Considering this systematic uncertainty, the agreement between calculated and observed VTDMs should be considered good.

## Acknowledgements



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