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Correlation Analysis of Optical Absorption Cross Section
and Rate Coefficient Measurements in Reacting Systems*

Jan P. Hessler**

Gas Phase Chemical Dynamics Group
Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

and

Paul J. Ogren

Department of Chemistry
Earlham College
Richmond, Indiana 47374

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**Author to whom correspondence should be addressed.

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Correlation analysis of optical absorption cross section and rate coefficient measurements in reacting systems*

Jan P. Hessler**

Gas Phase Chemical Dynamics Group, Chemistry Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439

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Paul J. Ogren

Department of Chemistry, Earlham College, Richmond, Indiana 47374

Predictions of the kinetics of complex reaction systems require accurate measurements of the rate coefficients over a wide range of temperature and pressure. These measurements are often obtained with optical techniques. For example, in combustion chemistry, shock tube methods are generally employed to generate high temperatures, and a variety of optical techniques are used to monitor the kinetic behavior of the atoms or radicals. Such techniques include absorption spectrophotometry with resonance lamps,^{1, 2} absorption measurements with spectrally narrow light from either a continuous-wave³ or pulsed⁴ dye laser, and resonantly induced fluorescence.⁵ All of these techniques measure a quantity which is proportional to the product of the optical absorption cross section and the concentration of the reacting species. Therefore, to determine this concentration the absorption cross section must be known for the temperature, pressure, and chemical composition used in the kinetic experiment. When a species is highly reactive, such as atomic H or O or the radicals OH, CH₃, or CH,

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a problem arises when measurements of the cross section are performed; it is difficult to prepare a known concentration of the reactive species. This concentration may depend critically upon the kinetic behavior of the observed species which, of course, is not precisely known.

Recently, we developed a technique for determining the relative importance of and correlation between reactions which make up a complex kinetic system.⁶ In this letter we apply this technique to investigate measurements of optical absorption cross sections and the correlation between cross sections and measured rate coefficients. From our analysis we conclude that (1) species, initial conditions, and temporal regions may be identified where cross sections may be measured without interference from the kinetic behavior of the observed species and (2) experiments designed to measure rate coefficients will always be correlated with the absorption cross section of the observed species. This correlation may reduce the accuracy of rate coefficient measurements.

Basically, the flux in an absorption experiment may be described by the equation

$$\Phi(z,t) = \frac{2\pi}{h\omega} \int_0^{\infty} I_0(\omega,t) \exp\{-\alpha(\omega,t)z\} d\omega. \quad (1)$$

The flux as a function of the distance along the optical path, z , and time, t , is $\Phi(z,t)$. The spectral intensity of the incident light is $I_0(\omega,t)$ where the angular frequency of the light is ω , the absorption coefficient is $\alpha(\omega,t)$, and Planck's constant is h . The absorption coefficient is often written in terms of the absorption cross section, $\sigma(\omega,T,P)$. For a spectrally narrow light source this gives

$$\alpha(\omega, t) = \sigma(\omega, T, P)n(t, T, P) = \frac{-1}{L} \ln \frac{\Phi(L, t)}{\Phi_0(L, t)} \quad (2)$$

The absorption cross section is a function not only of the angular frequency, but also the temperature, T , and pressure, P . The concentration of the species of interest is $n(t, T, P)$. The optical path length of the sample is L , the flux at the detector with the sample present is $\Phi(L, t)$, and the flux without the sample is $\Phi_0(L, t)$. Below, for convenience, we drop the functional dependence of T and P in the notation of the cross section.

To perform a correlation analysis of an optical absorption measurement performed on a complex chemical system we must calculate the matrix elements of the *discrimination* matrix. These matrix elements are given by equation (10) of reference 6, which is reproduced below.

$$D_{a_j a_k}(Z, \Delta t) = \sum_{i=1}^N \frac{a_j^* a_k^*}{Z_{\max}^2} S_{Z a_j}(t_i; a^*) S_{Z a_k}(t_i; a^*). \quad (3)$$

The dependent variable, Z , is measured over a time interval Δt ; $t_1 \leq t_i \leq t_N$. The set $\{a_1^*, \dots, a_M^*\}$ refers to the *best* values of the independent variables which are used to calculate the dependent variable. The sensitivity coefficients are $S_{Z j}(t_i; a^*)$ and $Z_{\max}$ is a constant value of the dependent variable which is chosen to simplify the equation to the product of *modified* reduced sensitivity coefficients. The discrimination matrix is dimensionless! To calculate the matrix elements we identify the generalized physical observable, Z , of equation (3) as the absorption coefficient, $\alpha(\omega, t)$, and calculate the sensitivity coefficients. In this case, the cross section is included with the rate coefficients in the set of independent variables, $\{a_1, \dots, a_M\}$ which determine the value of Z . This leads to the following sensitivity coefficients

$$S_{\alpha\sigma}(t_i; a^*) = \frac{\partial \alpha(\omega, t_i; a^*)}{\partial \sigma} = n(t_i, T, P; a^*). \quad (4)$$

and

$$S_{\alpha k_j}(t_i; a^*) = \frac{\partial \alpha(\omega, t_i; a^*)}{\partial k_j} = \sigma(\omega) \frac{\partial n(t_i, T, P; a^*)}{\partial k_j} \quad (5)$$

where k_j is a rate coefficient of the mechanism. Inserting equations (4) and (5) into equation (3) gives the diagonal element for the absorption cross section

$$D_{\sigma, \sigma}(\alpha, \Delta t) = \sum_{i=1}^N \frac{\sigma^2(\omega)}{Z_{\max}^2} n^2(t_i, T, P; a^*). \quad (6)$$

The off-diagonal elements which involve the cross section are

$$D_{\sigma, k_j}(\alpha, \Delta t) = \sum_{i=1}^N \frac{\sigma^2(\omega) k_j^*}{Z_{\max}^2} n(t_i, T, P; a^*) \frac{\partial n(t_i, T, P; a^*)}{\partial k_j}. \quad (7)$$

The matrix elements which do not involve the cross section are given by

$$D_{k_j k_m}(\alpha, \Delta t) = \sum_{i=1}^N \frac{\sigma^2(\omega) k_j^* k_m^*}{Z_{\max}^2} \frac{\partial n(t_i, T, P; a^*)}{\partial k_j} \frac{\partial n(t_i, T, P; a^*)}{\partial k_m}. \quad (8)$$

Since $Z_{\max} = \sigma(\omega)n(t_i = t_{\max}, T, P)$ where $t_{\max}$ is the time when the absorption coefficient is a maximum, the cross section terms cancel in each of the above matrix elements. Because of this, most of the terms in the discrimination matrix are identical to those obtained in the basic case where $Z = n(t, T, P)$, i.e. the case where the concentration of a species can be directly measured. The new discrimination matrix consists of the basic matrix (equation 8) plus an additional row and column of elements which involve the reduced sensitivity

coefficient for the cross section (equations 6 and 7). This coefficient is given by $n(t_1, T, P)/n(t_1 - t_{\max}, T, P)$ which is proportional to the concentration of the species and ranges from 0 to 1. This definition allows us to make direct comparisons between the reduced sensitivity coefficient for the cross section and coefficients for the rate constant of any reaction. Now that we have established the matrix elements of the discrimination matrix for an optical absorption experiment we may proceed with an analysis of the correlation between the absorption cross section and rate coefficients of a reaction mechanism.

To illustrate important aspects of correlations we consider measurements of a simple reaction where a precursor, P, dissociates in the low pressure limit to produce species A and B. We write the reaction as

with a rate coefficient k . The time dependence of the modified reduced sensitivity coefficients for the precursor are shown in fig. 1 and those for either product are shown in fig. 2. From a least-squares analysis of absorption data for the precursor one would determine the products $k[M]$ and $\ln(\sigma_P(\omega)L[P]_0)$ as the slope and intercept of the linear equation, $\ln(\alpha(\omega, t)L) = \ln(\sigma_P(\omega)L[P]_0) - k[M]t$. Therefore, as one would expect, both the absorption cross section and the rate coefficient for dissociation may be determined from a single experiment. Unfortunately, as with any linear equation, the values of the slope and intercept are correlated.⁷ This correlation can not be removed by any judicious choice of the temporal interval.

The situation is different if the absorption by either species A or B is measured. For this case, shown in fig. 2, the absorption profile provides information on $\sigma_{A \text{ or } B}(\omega)[P]_0$ without any correlation with $k[M]$ if the temporal period is chosen at long times, $4 < k[M]t_1$, where the sensitivity coefficient for

the reaction is very close to zero. If information on the product $k[M]$ is desired the data at early times, $k[M]t_{\max} < 4$, must be used. There will always be a correlation between $k[M]$ and $\sigma_{A \text{ or } B}(\omega)[P]_0$ but this correlation will go to zero as the length of the observation period is increased. This reduction is due to increased information on $\sigma_{A \text{ or } B}(\omega)[P]_0$ with little additional information about $k[M]$. From these two examples we can easily establish the criteria for optimal measurements of absorption cross sections: (1) the concentration of the species must be independent of time over a finite period, (2) during this period the concentration must be a maximum, and (3) the reduced sensitivity coefficients for all reactions must be equal to zero, or at least very small. Unfortunately, such criteria cannot be established for measurements of rate coefficients. It will be impossible to design an experiment to measure a rate coefficient without producing a reduced sensitivity coefficient for the cross section that will be near unity. Since the correlation between a rate coefficient and the cross section depends upon the product of their reduced sensitivity coefficients summed over the temporal interval of the measurement there will generally be some correlation between a measured rate coefficient and the optical absorption cross section of the observed species. The magnitude of this correlation will depend upon the relative magnitudes of the reduced sensitivity coefficients. In addition, we have observed situations where the cross section is the most sensitive parameter in a kinetic experiment. These situations occur when the magnitude of the reduced sensitivity coefficient for the cross section is always larger than the magnitude of the reduced sensitivity coefficient of each reaction.

To illustrate correlation in a more complex chemical system we show, in fig. 3, our low temperature measurements⁸ of the absorption profile of the

hydroxyl radical. Profiles such as this were used to measure the rate of the reaction $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$. The important reactions in this system are

The rate coefficients are most sensitive at the maximum slope of the absorption profile and the cross section is best determined at long times where the hydroxyl concentration is independent of the rate of formation of hydroxyl. In this illustration, the cross section may be determined without correlation with the rate coefficients for long times, $t \geq 40 \mu\text{s}$. The kinetic information is obtained from the interval $0 < t \leq 40 \mu\text{s}$. The normalized discrimination matrix for this interval is shown in Table I. As we might expect, the rate of reaction (2) dominates the shape of the absorption profile. The relative weight of this reaction is 54.3%. Perhaps a bit surprising is the relatively large weight for the cross section, 43.8%, and the small weight for reaction (6), 0.7%. The correlation between k_2 and σ may be expressed by

$$\frac{\delta k_2}{k_2} = \frac{1}{\tan \theta_{k_2, \sigma}} \frac{\delta \sigma}{\sigma} = -0.826 \frac{\delta \sigma}{\sigma} \quad (9)$$

where $\delta k_2 = k_2 - k_2^*$, $\delta \sigma = \sigma - \sigma^*$, and $\theta_{k_2, \sigma}$ is the angle which describes the correlation between k_2 and σ . This correlation implies that if a constant cross section were used in an analysis of the above profile and the cross section were shifted by some fraction, $\delta \sigma / \sigma$, from the value for the cross section at the conditions of the experiment, the calculated rate coefficient would be systematically shifted from the rate coefficient by -82.6% of the fractional shift in the cross section. This correlation must also be considered when

calculating the uncertainty in the measured rate coefficient. This uncertainty may be approximated by

$$\frac{\Sigma^2(k_2)}{k_2^2} - \frac{\Sigma_{\text{random}}^2(k_2)}{k_2^2} + 0.682 \frac{\Sigma^2(\sigma)}{\sigma^2} + 0.019 \frac{\Sigma^2(k_6)}{k_6^2} \quad (10)$$

where $\Sigma_{\text{random}}^2(k_2)$ is the variance associated with the random noise of the absorption profile used to determine the parameter k_2 , $\Sigma^2(\sigma)$ is the variance associated with the measurements of the cross section, and $\Sigma^2(k_6)$ is the variance associated with measurements of k_6 . The contributions to equation (10) from the uncertainties in the rate coefficient for reaction (-9) are insignificant.

An alternate way to obtain a more precise measure of correlations and to simultaneously obtain the most precise determination of both the cross section and rate coefficients is to perform a non-linear least-squares analysis of the absorption profile and allow the rate coefficients and cross section to vary. This approach will produce the *best-fit* values for all of the parameters. The *confidence limits* and correlations may then be determined by evaluating contours of constant $\Delta\chi^2$.⁹

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Table I. Normalized discrimination matrix for the absorption profile shown in figure 3.

Parameter	k_9	k_6	σ	k_2
k_9	0.007	-----	-----	-----
k_6	-----	0.010	-0.037	-0.074
σ	-----	-0.037	0.438	0.275
k_2	-----	-0.074	0.275	0.543

FIGURE CAPTIONS

- Fig. 1. Reduced sensitivity coefficients for the precursor of reaction (1). The solid line represents the coefficient for the cross section and the dashed line the rate constant of reaction (1).
- Fig. 2. Reduced sensitivity coefficients for either of the products of reaction (1). The solid line represents the coefficient for the cross section and the dashed line the rate constant of reaction (1).
- Fig. 3. Absorption profile of hydroxyl behind an incident shock wave, Mach No. = 5.121; post shock condition: $T = 2594 \text{ K}$, $P = 108.3 \text{ kPa}$; initial mole fractions: $\text{H}_2 = 3.98 \times 10^{-2}$, $\text{O}_2 = 4.21 \times 10^{-3}$, and $\text{Ar} = 0.956$.

Figure 1.

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Figure 2.

Figure 3.

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