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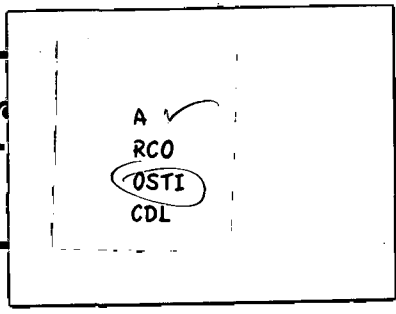
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COLLISION INDUCED ABSORPTION SPECTRA FOR GAS PHASE
CHEMICAL REACTIONS IN A HIGH POWER IR LASER FIELD

Ann E. Orel and William H. Miller

October 1979

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DISCLAIMER

Collision Induced Absorption Spectra

for Gas Phase Chemical Reactions in

a High Power IR Laser Field[‡]

By

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Abstract

A previously derived classical model for describing the interaction of molecular systems with high power IR lasers has been used to obtain the collision induced absorption spectrum of a state-selected, mono-energetic reactive collision system. The spectrum can be written as the Fourier transform of a particular dipole correlation function, and both the correlation function and the absorption spectrum are considered. Examples treated are a one-dimensional barrier problem, reactive and non-reactive collisions of $H + H_2$, and a modified $H + H_2$ potential surface that leads to a collision intermediate.

I.   Introduction

    We have shown in several recent papers[1] that high power infra-red lasers will in general enhance the rate of chemical reactions (by effectively lowering the activation energy) even if the reactant molecules themselves are infra-red inactive. This phenomenon is easily understood by considering the simple prototype reaction $H + H_2 \rightarrow H_2 + H$: although the reactant species have no dipole moment and are thus IR inactive, during a reactive collision the asymmetric stretch motion in the saddle point region of the potential energy surface, $\vec{H} \cdots \overset{\leftarrow}{H} \cdots \vec{H}$, will generate a time-varying dipole moment of the 3-atom system. This degree of freedom, which is essentially motion along the reaction coordinate, can thus absorb energy from the radiation field, and this accelerates the reaction.

    Previous studies[1] have focused on the effect the radiation field has on the molecular dynamics, i.e., changes in the reaction probability (or cross sections) caused by the laser, and this paper considers the converse, the effect the molecular dynamics has on the radiation field, i.e., the absorption and emission of photons from the field caused by the collision. More specifically, we consider in this paper the <u>collision induced absorption</u> (CIA) <u>spectrum</u> of a chemically reacting system. This is the analog of well-known non-reactive CIA,[2] the difference being the nature of the molecular collision process which gives rise to the absorption.

    The primary motivation for this kind of theoretical study is that reactively induced CIA is a means of observing <u>directly</u> the molecular mechanics in the transition state region of the potential energy surface. Thus unlike conventional scattering experiments, which can only prepare the system before collision and observe it after a complete collision,

this process interacts with the system while it is $\underline{in}$ the transition state region. The CIA spectrum is, in fact, infrared spectroscopy of the transition state. The two major aspects of the process which are considered in this paper are the special features which arise for $\underline{reactive}$ trajectories, compared to non-reactive ones, and the additional structure appearing in the spectrum when a collision complex is formed.

To see the qualitative differences between CIA spectra for reactive and non-reactive processes, Section II first treats a particle passing over (reactive), or being reflected by (non-reactive), a one-dimensional potential barrier. Section III then presents the results for a more realistic model, the collinear $H + H_2 \rightarrow H_2 + H$ reaction, and it is seen to show many features similar to the one-dimensional model of Section II. Finally, Section IV treats a modified $H + H_2$-like system, the modification being to introduce a potential $\underline{well}$ at the saddle point of the potential surface. This well causes some trajectories to form a short-lived collision complex, and the CIA spectrum shows new features related to this. Observation of the CIA spectrum would thus provide direct information about the $\underline{mechanism}$ of the reaction, i.e., whether it proceeds "directly" or through a short- or long-lived collision complex.

II. One Dimensional Barrier

This calculation was carried out, as were the calculations presented in later sections, within the framework of the classical theory[3] developed recently to treat the interaction of molecular systems with electromagnetic radiation. The usefulness of this classical model is that it provides a dynamically consistent description of the molecular system and of the radiation field and permits essentially exact (i.e., non-perturbative) calculations to be carried out. (Because the molecular dynamics is that of reactive scattering, a completely quantum mechanical treatment would be prohibitive.) Quantum effects could in principle be incorporated via classical S-matrix theory,[4] although the nature of such effects is well understood and are not expected to change any of the essential features of the results. Because of long-standing debates in the quantum optics community over whether or not a quantized radiation field is necessary to describe spontaneous emission, it was amusing (though actually quite trivial) to note[3,5] that this completely classical model also correctly describes spontaneous emission by molecular systems.

As shown in reference 3, the change in the energy of the radiation field during the collision is given by

$$(N_2 - N_1)\hbar\omega = \Delta N\hbar\omega =$$

$$\sqrt{\frac{8\pi\hbar\omega^3 N_1}{V}} \int_{t_1}^{t_2} dt\ \mu[\underset{\sim}{x}(t)]\ \cos[\omega(t-t_1) + Q_1]$$

$$+ \frac{2\pi\omega^2}{V} \left| \int_{t_1}^{t_2} dt\ e^{-i\omega t}\ \mu[\underset{\sim}{x}(t)] \right|^2 \tag{2.1}$$

where N_1, Q_1 are the initial number of photons and initial phase of the field, N_2 is the final number of photons, $\underset{\sim}{x}(t)$ is the molecular trajectory, $\mu[\underset{\sim}{x}(t)]$ is the component of the dipole moment along the polarization vector of the electric field as a function of time along the trajectory, ω is the frequency of the laser, V is the volume of the radiation cavity and t_1, t_2 are the initial and final times, respectively. The second term in Eq. (2.1) (which does not depend on N_1) is due to the classical analog of spontaneous emission[3] and for present purposes can be dropped.

Though this model allows the calculation of non-perturbative results, it is useful to consider the analytic expression obtained in the perturbative limit. If $\underset{\sim}{x}$ and $\underset{\sim}{p}$ denote the molecular coodinates and momenta, then the fractional change in the photon energy for initial conditions $(\underset{\sim}{x}_1, \underset{\sim}{p}_1)$ is

$$F(\omega) \equiv \frac{\Delta N}{N_1} = \frac{4\pi\omega}{V} \int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt' \, \sin[\omega(t'-t)]$$

$$\times \left[\frac{\partial\mu(t)}{\partial \underset{\sim}{p}_1} \cdot \frac{\partial\mu(t')}{\partial \underset{\sim}{x}_1} - \frac{\partial\mu(t)}{\partial \underset{\sim}{x}_1} \cdot \frac{\partial\mu(t')}{\partial \underset{\sim}{p}_1} \right] \quad . \tag{2.2}$$

By introducing the transformation

$$t' - t = \Delta t$$
$$t = t \quad ,$$

Eq. (2.2) can be written

$$F(\omega) = \frac{4\pi\omega}{V} \int_{0}^{\infty} d(\Delta t) \, \sin(\omega\Delta t) \, C(\Delta t) \quad , \tag{2.3}$$

where the correlation function $C(\Delta t)$ is

$$C(\Delta t) = \int_{-\infty}^{\infty} dt \; [\frac{\partial \mu(t)}{\partial \underset{\sim}{p}_1} \cdot \frac{\partial \mu(t-\Delta t)}{\partial \underset{\sim}{x}_1} - \frac{\partial \mu(t)}{\partial \underset{\sim}{x}_1} \cdot \frac{\partial \mu(t-\Delta t)}{\partial \underset{\sim}{p}_1}] \qquad . \tag{2.4}$$

The correlation function must be averaged over the appropriate distribution of initial conditions $(\underset{\sim}{x}_1, \underset{\sim}{p}_1)$. If this were a Boltzmann distribution, then $F(\omega)$ would be proportional to the standard expression[6] for the absorption coefficient of a molecular system and would always be positive. For a state- and energy-selected collision process, however, this average is only over the angle variables conjugate to the bound degrees of freedom. For a collinear A + BC collision, for example, with a specific initial translational energy and a specific initial vibrational state of BC, the average over initial conditions is only over the initial phase of the vibrational degree of freedom. As a consequence the averaged value $F(\omega)$ need not be positive.

To illustrate the qualitative nature of $C(\Delta t)$ and $F(\omega)$ as a function of laser frequency, a simple one-dimensional potential barrier was studied,

$$V(x) = -\frac{1}{2} m\omega_b x^2 \qquad . \tag{2.5}$$

The initial energy is given by

$$E_1 = \frac{p_1^{\,2}}{2m} - \frac{1}{2} m\omega_b^{\,2} x_1^{\,2} \qquad , \tag{2.6}$$

and the trajectory is reactive or non-reactive for $E_1 > 0$ or $E_1 < 0$, respectively; cf. Figure 1. The field-free trajectory is given by

$$x_0(t) = x_1 \cosh(\omega_b t) + \frac{P_1}{m\omega_b} \sinh(\omega_b t) \quad , \tag{2.7}$$

and dipole moment $\mu(x)$ selected for the calculation was

$$\mu(x) = x \operatorname{sech}^2 x \quad . \tag{2.8}$$

Choosing ω_b ($=.001$ atomic unit), m ($= 1$ amu) and x_1 ($= -10.0$ a_0, large enough that $\mu(x) \approx 0.0$) allows $C(\Delta t)$ and $F(\omega)$ to be calculated for a series of fixed initial energies E_1. Figures 2 and 3 show typical results for the case of a non-reactive (NR) trajectory ($E_1 = -0.1$ eV) and a reactive (R) trajectory ($E_1 = 0.1$ eV). For both $C(\Delta t)$ and $F(\omega)$ the NR result is very similar to conventional[2] collision induced absorption spectra in non-reactive systems, but the R case is seen to be qualitatively different: depending on the laser frequency ω, the molecular system can either gain energy from or lose energy to the radiation field. This was also indicated in previous studies[1] where, depending on the translational energy and laser frequency, the reaction probability was either increased or decreased.

III. Classical Trajectory Calculations for $H + H_2 \rightarrow H_2 + H$.

To obtain a more quantitatively reliable characterization of the correlation function and its corresponding collision induced absorption spectrum, classical trajectories were carried out for the collinear $H + H_2$ reaction within the framework of the theoretical model in reference 3. The classical Hamiltonian for the complete system, molecular system plus radiation field, is

$$H(p,r,P,R,N,Q) = \frac{P^2}{2\mu} + \frac{p^2}{2m} + V(r,R) + \hbar\omega(N + \tfrac{1}{2})$$

$$- \sqrt{\frac{8\pi\hbar\omega N}{V}} \; \mu(r,R) \; \sin Q \quad , \tag{3.1}$$

and the initial conditions for the trajectories are

$$R(t_1) = \text{large}$$

$$P(t_1) = -\sqrt{2\mu E_1}$$

$$N(t_1) = N_1$$

$$Q(t_1) = Q_1$$

$$r(t_1) = r(n_1, q_1)$$

$$p(t_1) = p(n_1, q_1) \tag{3.2}$$

where $r(n_1, q_1)$, $p(n_1, q_1)$ are the algebraic functions expressing the vibrational variables (r,p) in terms of the vibrational action-angle variables (n,q). In Eq. (3.1) $V(r,R)$ is the potential energy surface and $\mu(r,R)$ the dipole moment of the $H + H_2$ system. For the potential

energy surface a modified LEPS (London-Eyring-Polanyi-Sato) function was used, the parameters of which are summarized in Table I. The dipole moment function was taken to be

$$\mu(r,R) = \mu_0 \ s \ sech^2 s \quad , \tag{3.3}$$

where $s = \frac{3}{2} \ r-R$ is the asymmetric stretch coordinate at the saddle point of the potential surface. This form for the dipole moment is qualitatively correct, although there is no reason to believe that it is quantitative. Within the perturbative limit the constant μ_0 enters as simply a multiplicative constant in $C(\Delta t)$ and $F(\omega)$.

The CIA spectrum $F(\omega)$ is given in an exact calculation by

$$F(\omega) = (N_1 \hbar \omega)^{-1} \sqrt{\frac{8\pi\hbar\omega^3 N_1}{V}} \ (2\pi)^{-2} \int_0^{2\pi} dq_1 \int_0^{2\pi} dQ_1$$

$$\times \int_{t_1}^{t_2} dt \ \mu[\underset{\sim}{x}(t)] \ cos[\omega(t-t_1) + Q_1] \quad , \tag{3.4}$$

where $\underset{\sim}{x}(t)$ is the molecular trajectory determined by integrating Hamilton's equations (generated from the Hamiltonian in Eq. (3.1)) with the initial conditions of Eq. (3.2). In a perturbative calculation only the field-free trajectory is calculated. This corresponds to the following equations of motion:

$$\dot{R} = \frac{\partial H}{\partial P} = P/\mu$$

$$\dot{P} = -\frac{\partial H}{\partial R} = -\frac{\partial V}{\partial R}$$

$$\dot{r} = \frac{\partial H}{\partial p} = p/m$$

$$\dot{p} = -\frac{\partial H}{\partial r} = -\frac{\partial V}{\partial r} \quad . \tag{3.5}$$

However since the derivatives of the dipole moment with respect to the initial conditions as a function of time are also necessary, the additional equations of motion governing the derivatives of the dynamical variables with respect to the initial conditions must also be integrated. These are[7]

$$\frac{d}{dt} [\underset{\sim}{R}(t)] + [\underset{\sim}{F}(t) \cdot \underset{\sim}{R}(t)] = 0 \tag{3.6}$$

where

$$\underset{\approx}{R}(t) = \begin{pmatrix} \dfrac{\partial \underset{\sim}{q}(t)}{\partial \underset{\sim}{q}_1} & \dfrac{\partial \underset{\sim}{q}(t)}{\partial \underset{\sim}{p}_1} \\[3mm] \dfrac{\partial \underset{\sim}{p}(t)}{\partial \underset{\sim}{q}_1} & \dfrac{\partial \underset{\sim}{p}(t)}{\partial \underset{\sim}{p}_1} \end{pmatrix}$$

$$\underset{\approx}{F}(t) = \begin{pmatrix} -\dfrac{\partial^2 H}{\partial \underset{\sim}{p} \partial \underset{\sim}{q}} & -\dfrac{\partial^2 H}{\partial \underset{\sim}{p}^2} \\[3mm] \dfrac{\partial^2 H}{\partial \underset{\sim}{q}^2} & \dfrac{\partial^2 H}{\partial \underset{\sim}{q} \partial \underset{\sim}{p}} \end{pmatrix}$$

where $R(t_1)$ is the unit matrix. This information allows the construction of $C(\Delta t)$ via[Eq. (2.3)], which is Fourier sine-transformed [Eq. (2.13)] to obtain $I(\omega)$. As in the exact case $C(\Delta t)$, and hence $I(\omega)$, requires an average over initial conditions, which in the case of the collinear perturbative result is just an average over the initial phase of the BC oscillator.

A typical correlation function generated by non-reactive trajectories is shown in Figure 4. (The initial vibrational state $n_1=0$, the translational energy $E_1 = 0.1$ eV, and all trajectories in this case are non-reactive.) The overall shape is basically the same as the NR correlation function in Figure 2 except for a superimposed high frequency oscillation. This oscillation is due to changes in the dipole moment caused by the H_2 vibrational motion relative to the incoming H [Eq. (3.3)]. The absorption spectra (calculated perturbatively) is shown in Figure 5. There are two peaks, one at low frequency due basically to translational motion and one at high frequency (at the H_2 vibrational frequency). The spectrum was also computed non-perturbatively and found to agree well with the perturbative calculation.

Figures 6 and 7 show the correlation function and corresponding absorption spectrum, respectively, which are determined from reactive trajectories of $H + H_2$. (In this case $n_1=0$, $E_1=0.30$ eV and 94% of the trajectories are reactive.) One again sees a high frequency oscillation in $C(\Delta t)$ which comes from vibration of H_2, and apart from this the correlation function and spectrum are similar to the reactive case of the one-dimensional model of Section II.

Referring to the absorption spectra in Figures 5 and 7, one sees that the collision system will absorb frequencies in the vicinity of the

H_2 vibrational frequency. The collisional perturbation induces a dipole in H_2 and thus makes it IR active, and such an effect would exist for any collision partner. Wormer and Van Dijk,[8] for example, have recently carried out calculations for absorption in H_2 induced by collision with He atoms.

Absorption at the lower frequencies (cf. Figures 5 and 7), however, is more relevant to the process of our interest; it is related to translational motion along the reaction coordinate. It is this region of the absorption spectrum, therefore, that is most closely related to the reaction dynamics.

IV. Model for a Short-Lived Collision Intermediate

To investigate the sensitivity of the correlation function and absorption spectrum to the reaction dynamics, the $H + H_2$ potential energy surface was modified by introducing a well at the top of the potential barrier. This causes H and H_2 to form a short-lived collision intermediate, i.e., some trajectories oscillate several times in the vicinity of the well before passing on to products (or back to reactants).

The potential surface used in the calculation was the LEPS surface described in the previous section plus an additional term V_{well}, where

$$V_{well} = c \, e^{-\alpha[(R_1-c_1)^2 + (R_2-c_2)^2]}$$

where α, c, c_1, c_2 are constants and R_1, R_2 are the interatomic distances. For this calculation, $c_1 = c_2 = 1.7574 \, a_0$, $\alpha = 1.0$ and $c = -0.01$ which placed a gaussian well at the saddle point. The frequencies of the normal modes associated with the bottom of the well are $\omega_1 = 0.008$ and $\omega_2 = 0.010$ (atomic units).

The correlation function for this system is shown in Figure 8 for a translational energy of 0.1 eV. Due to the changes in the surface caused by the well $\sim$ 82% of the trajectories reacted, $\sim$ 36% remained in the well for one or more complete vibrations, $\sim$ 14% for two or more complete vibrations and $\sim$ 2% for three complete vibrations. Due to these effects the correlation function has more structure than in the calculation without the well, and it retains a high frequency oscillation due to the H_2 vibration.

Figure 9 shows the absorption spectrum, which also shows considerably more structure. This spectrum is essentially that of the collision complex,

and one does, in fact, see peaks at ω_1 and ω_2, the harmonic frequencies related to the potential well, as well as peaks of $2\omega_1$ and $\omega_1 + \omega_2$. There are other peaks, however, which are not readily identified in terms of the harmonic frequencies. Since the potential well is shallow and very anharmonic, this is not surprising.

If the collision complex were long-lived, one would expect to see much sharper lines in the absorption spectrum. From these one could in principle determine the geometry and force constants of the collision intermediate.

V.   Concluding Remarks

We have given the basic equations (cf. Section II) which relate the CIA absorption spectrum for a state-selected, mono-energetic collision system to a particular dipole correlation function. A Boltzmann average over initial states and collision energy converts these expressions into the standard ones.[6]

The first application of these formulae (Section II) was to a particle moving in one dimension over, or being reflected by, a potential barrier. Application (in Section III) to a more realistic model of a chemical reaction, collinear $H + H_2$, showed that the qualitative behavior seen in the one-dimensional model also appears in the more realistic model.

Finally, the model treated in Section IV showed how the CIA spectrum is changed when the reaction mechanism involves the formation of a collision intermediate. It is effects such as this that would make experimental observation of these spectra   informative of the reaction dynamics.

Acknowledgments

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‡. A preliminary version of these results was presented at the XI International Conference on the Physics of Electronic and Atomic Collisions, Kyoto, Japan, August 29–September 4, 1979.

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Table 1. LEPS parameters for $H + H_2$ potential energy surface.

D_e(kcal/mole)	109.5
$\beta(\overset{\circ}{A}{}^{-1})$	1.942
$r_0(\overset{\circ}{A})$	0.7417
Δ	0.1413

Figure Captions

1. A one-dimensional parabolic barrier indicating the initial position x_1 and initial energy E_1.

2. Correlation function $C(\Delta t)$ for the one-dimensional barrier in the reactive (R, $E_1 > 0$) and non-reactive (NR, $E_1 < 0$) cases.

3. Absorption spectrum corresponding to the correlation function in Figure 2.

4. Correlation function for non-reactive trajectories of the collinear $H + H_2$ collision.

5. Absorption spectrum corresponding to the correlation function in Figure 4.

6. Correlation function for reactive trajectories of the collinear $H + H_2$ collision.

7. Absorption spectrum corresponding to the correlation function in Figure 6.

8. Correlation function for the modified $H + H_2$ potential surface.

9. Absorption spectrum corresponding to the correlation function in Figure 8.

XBL 7812-14071

Fig. 1

Δt (atomic units) $\times 10^{-3}$

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Fig. 2

ω (atomic units)$\times 10^3$

XBL 7911-12746

Fig. 3

Fig. 4

XBL 7911-12749

XBL 7911-12745

Fig. 5

$$\Delta t \times 10^{-2} \text{ (atomic units)}$$

XBL 7911-12747

Fig. 6

ω (atomic units) $\times 10^3$

F(ω) (arbitrary units)

XBL 7911-12744

Fig. 7

Fig. 8

XBL 7911-12748

Fig. 9

XBL 7911-12743