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Collisional energy transfer from excited polyatomic molecules produced by infrared multiple photon absorption

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A simple energy-grained master equation is used to model data on the multiphoton dissociation of CF_2HCl as a function of laser fluence and argon bath-gas pressure. Information on energy transfer from vibrationally excited CF_2HCl is obtained from an analysis of the competition between laser pumping and collisional energy removal using suitable parametrizations of the laser intensity and the collision process.

INTRODUCTION

Master equations have been widely used to study collisional processes in thermal and photochemical systems,¹ and recently have found application in understanding the process by which polyatomic molecules undergo infrared multiple-photon absorption under collisionless conditions.^{2,3} In this paper we show that under collisional conditions the competition between laser pumping and collisional energy transfer can be used to derive information on energy transfer. This is done by adding collisional terms to the simple energy-grained master equation (EGME) often used to model multiphoton dissociation experiments.

The collisional EGME is applied to recent data by Duperrex and van den Bergh⁴ on the multiphoton dissociation of CF_2HCl as a function of laser fluence and argon bath-gas pressure. We show that pressure-dependent data of this type are particularly useful for master equation modeling, because certain effects on the pumping process that make the simple EGME invalid are removed in the presence of collisions. For instance, the depletion of a particular subset of molecules which is easily pumped, or the occurrence of pumping steps with rates that cannot be represented by simple terms linear in intensity, does not occur under collisional conditions.

The collisional terms in the EGME are independent of the laser intensity; thus, it is necessary to consider in detail the temporal intensity dependence of the laser to accurately represent the competition between laser pumping and collisional energy removal. Various methods of parametrizing the laser intensity are discussed later.

THE ENERGY-GRAINED MASTER EQUATION

The EGME of the type shown in Eq. (1) has been extensively used to model data on collisionless multiphoton dissociation²:

$$\frac{dN_m}{dt} = C_{m-1}^a N_{m-1} + C_m^e N_{m+1} - C_m^a N_m - C_{m-1}^e N_m - k_m N_m, \quad (1)$$

where N_m is the population in the m th level (m photons absorbed), C_m^a is the effective first-order rate constant

for absorption from level m to $m+1$, and C_m^e is the effective first-order rate constant for stimulated emission from level $m+1$ to m . Thus,

$$C_m^a = \sigma_m I(t)/h\nu \text{ and } C_m^e/C_m^a = g_m/g_{m+1},$$

where σ_m is the effective absorption cross section for the m to $m+1$ transition, $I(t)$ is the laser intensity, $h\nu$ is the photon energy, g_m is the molecular density of states at energy $m h\nu$, and k_m is the unimolecular decomposition rate constant at energy $m h\nu$.

The simple EGME (1) describes the multiple-photon absorption process as a series of incoherent sequential one-photon transitions between a set of equally spaced energy levels. Numerical solutions of Eq. (1) show that the product yield depends almost completely on the laser fluence, the integrated intensity over the laser pulse length, and not the absolute value of the intensity.

The first quantitative data on collisionless multiphoton decomposition for SF_6 showed good agreement with the EGME.² There was little intensity dependence in the yield at constant fluence; and the yield as a function of fluence was well represented by the solution of Eq. (1) with a physically reasonable model for the energy dependence of the absorption cross sections.³ However, later experiments on other molecules have shown departures from this expected behavior, significant intensity dependence in the dissociation yield, and average number of photons absorbed.^{5,6} This may be due to a number of effects. Coherent absorption processes, incoherent absorption with a sparse density of states, and nonhomogeneous populations of absorbing molecules have been suggested. Quack² has also discussed situations (Case C in Ref. 2) in which the pumping process is nonlinear in intensity. In these cases, the EGME is not correctly representing the transitions in the first few levels where such effects should be important. This is because these transition rates cannot be given by terms linear in intensity, or because only a certain fraction of the molecules are interacting with the laser. This fraction may also be dependent on the laser intensity. The effects are often referred to as a discrete level, or early bottleneck situation.

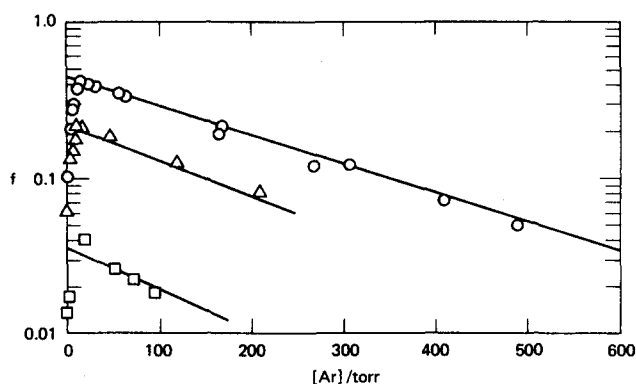


FIG. 1. Experimental results for the multiphoton dissociation of CF_2HCl . Fluence: $\circ = 6 \text{ J/cm}^2$; $\Delta = 4 \text{ J/cm}^2$; $\square = 2.2 \text{ J/cm}^2$. The lines were calculated as described in the text using the parameter $\sigma_m = 3.6 \times 10^{-18} (m+1)^{-1.4} \text{ cm}^2$, $-\langle \Delta E \rangle = 0.1 \text{ kcal mol}^{-1}$.

Under collisional conditions, transitions across the discrete level bottleneck can be facilitated to such an extent that a single EGME is a good representation of the laser-pumping process for all of the molecules.

COLLISIONAL MODELS

Collisional energy-transfer studies using a master equation approach have been extensively reviewed by Tardy and Rabinovitch⁷ and by Troe.⁸ Following their approaches, we add collisional terms to the right-hand side of Eq. (1), given by $Z_{LJ} N_j [A] \sum_i P(i/j)$, where Z_{LJ} is the Leonard-Jones collision rate constant between the reactant and the bath gas, $[A]$ is the concentration of bath gas, and $P(i/j)$ is the probability that a reactant molecule in state j before collision is in state i after collision. In order to maintain computational tractability, we must maintain the energy grain size in the EGME at about one photon. Thus, we need to represent $P(i/j)$ as the probability that a molecule of energy $m h \nu$ before collision has an energy $(m \pm 1) h \nu$, $(m \pm 2) h \nu$, ..., after collision. Also, in the collisional case, reactant molecules may contain a continuous range of energies, not just the energy of an integral number of photons. To accommodate this, we consider that all molecules with energy between $(m \pm \frac{1}{2}) h \nu$ are in level m . Thus, we require the probability that a molecule with energy between $(m \pm \frac{1}{2}) h \nu$ before collision has an energy between $(m + \frac{1}{2}) h \nu$ and $(m + 1.5) h \nu$, i.e., (P_{up}); or between $(m - \frac{1}{2}) h \nu$ and $(m - 1.5) h \nu$, i.e., (P_{down}), after collision, allowing only for nearest-neighbor transitions. Thus, Eq. (1) becomes

$$\begin{aligned} \frac{dN_m}{dt} = & C_{m-1}^a N_{m-1} + C_m^e N_{m+1} - C_m^a N_m - C_{m-1}^e N_m - k_m N_m \\ & - Z_{LJ} N_m [A] P_{\text{up}} - Z_{LJ} N_m [A] P_{\text{down}} \\ & + Z_{LJ} N_{m-1} [A] P_{\text{up}} + Z_{LJ} N_{m+1} [A] P_{\text{down}} . \end{aligned} \quad (2)$$

We now require a model for the collisional transition probabilities. Many different models have been suggested, but an exponential form has been most widely used. We use the exponential model of Troe^{1,8} to facilitate comparison of our results with his extensive work in thermal unimolecular reactions. We define $P(E'/E)$,

the probability that a molecule with energy E before collision has energy E' after collision, as

$$P(E'/E) = \frac{1}{N} \begin{cases} \exp[-(E-E')/\alpha] , & \text{for } E' < E , \\ \exp[-(E'-E)/\beta] , & \text{for } E' > E . \end{cases} \quad (3)$$

N is a constant normalization factor given by $(\alpha + \beta)$ and α and β are constants related by detailed balancing. The $P(E'/E)$ are characterized by suitable averages, most commonly the average energy transferred in all collisions $\langle \Delta E \rangle$, which is given by $(\beta - \alpha)$. In our case, we require the probability that molecules in a given energy range before collision are in another given energy range after collision; thus,

$$\begin{aligned} P_{\text{up}} &= \int_{(m-1/2)h\nu}^{(m+1/2)h\nu} \int_{(m+1/2)h\nu}^{(m+3/2)h\nu} P(E'/E) dE dE' , \\ P_{\text{down}} &= \int_{(m-1/2)h\nu}^{(m+1/2)h\nu} \int_{(m-3/2)h\nu}^{(m-1/2)h\nu} P(E'/E) dE dE' . \end{aligned} \quad (4)$$

For a given value of $\langle \Delta E \rangle$, α and β may be calculated, and the above integrals evaluated. Note that P is independent of the energy content of the colliding molecules. Also, for reasonable values of $\langle \Delta E \rangle$, the non-nearest-neighbor transition probabilities (P') are unimportant:

$$P' = \int_{(m-1/2)h\nu}^{(m+1/2)h\nu} \int_{(m\pm 5/2)h\nu}^{(m\pm 7/2)h\nu} P(E'/E) dE dE' \approx 0 .$$

In using a coarse grain size for the collisional behavior, we are assuming that the energy transfer behavior and the population density are uniform across the grain. The first assumption is implicit in the energy transfer model, but the second involves the approximation that we can represent a smooth curve (the actual population distribution with energy) by a series of step functions.

RESULTS

The experimental results, the fractional decomposition (f) of CF_2HCl as a function of laser fluence and bath gas (Ar) pressure, are shown as the points in Fig. 1. The experimental details have been extensively discussed elsewhere.⁴ The linear decrease of $\log f$ with increasing bath gas pressure has been observed before for SF_6 ,⁹ and seems to be generally true. Clearly, in this region collisional energy transfer is competing with the laser-pumping process, and the information we wish to recover is contained in the slope of the line.

The initial increase in f with added bath gas has also been observed with SF_6 , although the effect was much smaller for SF_6 (Ref. 9) at the applied conditions. This behavior is consistent with the early bottleneck picture. Similarly, SF_6 shows a weak intensity dependence,¹⁰ whereas CF_2HCl shows a strong intensity dependence.⁶ An unambiguous analysis of the role of collisions in this initial region is not possible since the origin of the bottleneck and the mechanism by which the transitions across the first discrete levels take place are not easy to analyze in a quantitative manner. However, it seems clear that collisions facilitate transitions across the first discrete levels and that if this were the only effect occurring, increasing the pressure would increase the

yield until a point at which the simple EGME would be a valid description of the behavior of all the molecules and the yield would depend only on the laser fluence. This is not observed because increasing the pressure also results in increased net collisional energy transfer from the laser-pumped molecules causing a decrease in the yield. Thus, the yield goes through a maximum as observed. However, if the linear section is extrapolated back to the ordinate, it should yield the fractional yield under collisionless conditions in the absence of any bottleneck in the lower discrete levels. This is confirmed experimentally using different bath gases.^{9,11} In this case, at a given fluence, straight lines of different slopes are obtained for different bath gases, indicating different energy transfer efficiencies, but all the lines extrapolate back to the same point as predicted.

The variation of f , determined by extrapolation as above, with fluence should be well represented by the simple EGME (1). We use this information to determine the laser-pumping rate by numerical solution of Eq. (1) with various models for σ_m , the energy-dependent absorption cross section which is the only unknown. The molecular density of states g_m is calculated by direct count of the vibrational states. Under collisional conditions the actual molecular density of states is slightly higher than the vibrational density due to collisional coupling of the rotational states, but this would have a negligible effect on the calculations. The values of k_m are calculated from RRKM theory [$k_m(m < 18) = 0$]. For a small molecule, such as CF_2HCl , the RRKM rate constant increases very rapidly with energy above the threshold, so that all molecules dissociate within two or three levels of the threshold. The computational results are therefore insensitive to the exact values of k_m .

The experimental data are well represented by the solution of Eq. (1), if σ_m has the form $\sigma_m = \sigma_0(m+1)^{-n}$, when $n = 1.4$ and $\sigma_0 = 3.6 \times 10^{-18} \text{ cm}^2$. The derived value of σ_0 is a factor of 3 higher than the measured value at the appropriate wavelength. In view of the fact that the functional form of the energy dependence is a considerable simplification of the real situation, this must be considered good agreement.

Having determined σ_m above, we may now solve the master equation, including collisional effects (2). This equation now contains one adjustable parameter, the average energy transferred in all collisions $\langle \Delta E \rangle$, which determines P_{up} and P_{down} . However, the solution of Eq. (2) requires a knowledge of $I(t)$, the time dependence of the laser intensity which was not needed for the solution of Eq. (1). To clarify, all the terms on the right-hand side of Eq. (1) depend linearly on I (except the decomposition term which does not perturb the ladder-climbing process); thus, one may divide through by I and show that the solution depends only on $\int_0^t I(t) dt$, not $I(t)$, itself, i.e., the result for the collisionless case depends only on the laser fluence, or total energy, not the rate at which this energy is deposited. The experimental results under collisionless conditions do show an intensity dependence because the transitions across the discrete early levels cannot be described by simple terms linear in intensity. Extrapolating the collisional results

back to zero pressure removes this experimental intensity dependence and makes Eq. (1) applicable. In the collisional regime, a second type of intensity dependence is produced because some of the terms on the right-hand side of Eq. (2) are not linearly dependent on I . Thus, the solution of Eq. (2) depends explicitly on $I(t)$ even though it represents all the optical pumping terms as simple incoherent one-photon transitions linear in I .

Equation (2) may be integrated if we can represent the time dependence of the laser intensity in some convenient manner. There is some difficulty here because examination of the laser output shows it to be a variable series of spikes, not a smooth envelope. We estimate that the duty cycle of the laser is approximately 50% although there is considerable variation within and between laser pulses. We represent this behavior as a series of 50 ns rectangular laser pulses separated by 50 ns intervals in which the intensity is zero. The parametrized intensity is calculated from the measured total energy and the intensity envelope,⁴ such that over a calculated 100 ns interval (50 ns laser on and 50 ns laser off), the measured amount of energy has been deposited. The laser spike width is probably ~ 5 ns, but it is computationally simpler to group the spikes in 50 ns intervals, and the computed behavior over ~ 100 or 200 ns intervals is identical.

Using the above laser parameterization and σ_m determined previously, we numerically integrate Eq. (2) with various values for $\langle \Delta E \rangle$. This yields (for each fluence in Fig. 1) a series of straight lines of different slope, passing through the same point on the ordinate. The collisional master equation, therefore, predicts the observed linearity of the $\log f$ against pressure plots; furthermore, at a value of $-\langle \Delta E \rangle = 0.1 \text{ kcal mol}^{-1}$, the predicted lines agree well with experiment over a wide pressure range. The results of this calculation are shown as the lines in Fig. 1. The value of f was determined by integration of Eq. (2) for a time longer than the laser pulse ($I = 0$ after the laser pulse), such that the molecules above the reaction threshold at the end of the laser pulse could dissociate or be collisionally quenched.

It is instructive to consider what effect our parameterization of the laser pulse has on the results. If we assume that the pulse envelope represents the true intensity (duty cycle 100%), we find similar straight line behavior in the $\log f$ against pressure plots. However, here there is no value for $\langle \Delta E \rangle$ that will produce the observed slopes at all fluences. For instance, adjusting $\langle \Delta E \rangle$ to fit the results at 4 J/cm^2 gives lines too steep at 2.2 J/cm^2 . Reducing the duty cycle to 5% (5 ns laser on, 95 ns laser off) has a much smaller effect on the results; essentially identical behavior to that shown in Fig. 1 is obtained for $-\langle \Delta E \rangle \approx 0.12 \text{ kcal mol}^{-1}$.

One further comparison of the collisional master equation and experiment is possible. This is shown in Fig. 2. The measured time dependence of the formation of the CF_2 dissociation product is compared with the solution of the master equation using the same parameters as for Fig. 1. The agreement is very good, confirming the validity of our approach.

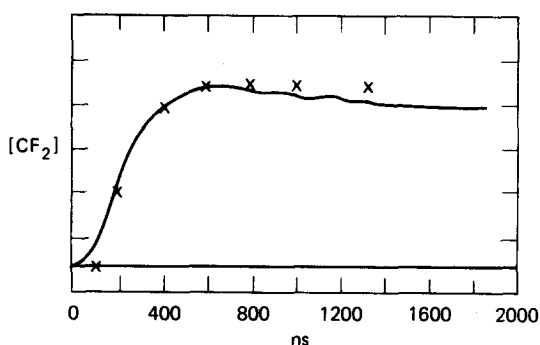


FIG. 2. Experimental result for the time-dependent appearance of the CF_2 product from the multiphoton dissociation of CF_2HCl at 6 J/cm^2 in 80 Torr Ar (line). The points were calculated using the parameters given in Fig. 1, and the model described in the text.

DISCUSSION

It has been shown that a simple extension of the EGME will accurately reproduce the observed results in multiphoton dissociation under collisional conditions. We may compare our derived value for the average energy transferred by collision with argon to values derived from other studies. In general, information on energy transfer from polyatomic molecules is obtained in two other types of experiments. Thermal experiments, in which the rates of unimolecular decomposition, or the reverse recombination, reactions in the low pressure limit are analyzed using a master equation approach, and nonthermal experiments in which molecules are chemically or photochemically activated above their reaction threshold energies, and the extent of reaction relative to collisional energy transfer are measured. These two types of experiment sample different collisional energy-transfer processes. The thermal experiments sample collisions between thermally equilibrated reactants and bath gas molecules over a range of energies up to approximately the reaction threshold. In chemical and photochemical activation, a narrow non-thermally equilibrated distribution of reactant molecules above the reaction threshold is produced, and collisions over the energy range above the threshold are sampled. The information derived in these experiments represents a complex average of two effects: the collisional relaxation towards a thermal distribution of the initially monoenergetic reactants and the net collisional energy transfer to the bath gas. The results derived from thermal and nonthermal activation studies show considerable variation between different experiments. However, two surprising general conclusions can be drawn. First, the value for $\langle \Delta E \rangle$ shows no systematic variation with the type of activation, and second, the value of $\langle \Delta E \rangle$ depends only on the bath gas, not the reactive substrate.

Our experiments on collisional energy transfer in multiphoton-excited molecules are in many ways intermediate between the two types of experiment described above. In common with thermal experiments, we are sampling collisions over an energy range up to the re-

action threshold, but in common with the chemical and photochemical experiments we are sampling collisions between non-thermally equilibrated reactants and the bath gas, and relaxation as well as net energy transfer takes place. Our numerical result for argon of $-\langle \Delta E \rangle = 0.1 \text{ kcal mol}^{-1}$ may be compared with values of $0.4 \text{ kcal mol}^{-1}$ at 300 K and $0.2 \text{ kcal mol}^{-1}$ at 3000 K derived by Troe⁸ from an analysis of a large amount of data on thermal low-pressure limit reactions, and typical values of $-\langle \Delta E \rangle \approx 0.5\text{--}1.0 \text{ kcal mol}^{-1}$ found in chemical and photochemical activation studies. Our value is seen to be somewhat lower than the consensus. This is not entirely unexpected as argon has been observed to be particularly inefficient in energy removal in multiphoton experiments. Results on the multiphoton dissociation of SF_6 (Ref. 9) and CF_2HCl (Ref. 11) show that on a per collision basis, argon is a less efficient collider than helium at room temperature. This is the reverse of observations in nonmultiphoton experiments at room temperature, although there is some evidence that at high temperatures argon may be less efficient than helium.¹² The reasons for this relative change in efficiency are not known, and more detailed studies of energy transfer in multiphoton systems may shed some light on this interesting problem. The multiphoton studies, in conjunction with other types of activation, should yield complementary information on the relative importance of vibrational-to-translational and rotational equilibration of the substrate compared to the net energy transfer to the bath gas molecule.¹³ In the multiphoton experiments, the analysis would be considerably simplified by the use of smooth mode-locked laser pulses, which should be used if possible.

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¹³It remains to be seen whether this behavior can be characterized by a simple average energy transferred per collision, and if the values of $\langle \Delta E \rangle$ derived here have the same significance as those of Refs. 7 and 8.