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A quantitative test of unimolecular rate theory in the multiphoton dissociation of CF$_2$CFCI

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We have measured the distribution of total energy in reaction products for the CO$_2$ laser-induced MPD: CF$_2$CFCI→CF$_2$ + CFCI. From a separate study of MPD rates as a function of laser intensity and inert buffer gas pressure, reliable estimates of the radiative pumping rates are known for this reaction. These results, when analyzed together, allow us to extract a unimolecular A-factor from the MPD data. The determined value $A = 3 \times 10^{10}$ sec$^{-1}$ agrees well with estimates based on independent thermal data.

INTRODUCTION

In multiphoton dissociation (MPD) experiments a single molecule can adsorb 30, 40, or more IR photons, thereby obtaining a total internal energy $E$ in excess of the threshold energy $E_0$ required for unimolecular decay. The excited ($E > E_0$) molecule then either decays or again interacts with the radiation field by absorbing, or possibly emitting, another photon. The relative probability of these two events is determined by the ratio, unimolecular decay rate to radiative pumping rate. In this aspect MPD is very similar to the well studied thermal unimolecular reaction in which a molecule is occasionally excited by collision into the very high energy tail of the Boltzmann distribution. The thermally excited ($E > E_0$) molecule then either decays or again collides with another molecule; the relative probability being determined by the ratio, unimolecular decay rate to collision rate.

Because of this similarity in the two processes one expects quantitative correlations between relevant data obtained from MPD and thermal unimolecular experiments. More specifically, one seeks quantitative tests of the applicability to MPD of the RRKM, or the simplified RRK, theory for unimolecular decay rates as a function of internal energy. RRKM theory already successfully correlates a large body of thermal unimolecular reaction data. The RRKM and RRK theories, like the statistical theory of nuclear reaction, assume rapid randomization of energy among internal degrees of freedom. Thus a sufficiently tight test of RRKM or RRK theory in MPD is also a test of the energy randomization hypothesis with obvious implications for the possibility of selective chemistry.

Conventional MPD experiments have not provided any quantitative comparisons with results known from thermal unimolecular theory, because: (i) Experiments which measure the total product yield are inherently insensitive to the microscopic unimolecular decay constants. In effect they simply measure the efficiency of pumping molecules into reactive states. (ii) In the more sophisticated time resolved and pressure fall-off experiments, of the type which we and others have analyzed, most molecules get pumped up to that level which has sufficient energy so that unimolecular decay competes with radiative pumping between reactive levels. In effect these experiments measure the rate of radiative pumping between reactive states. (iii) In the important experiments of Lee and coworkers the critical assumption of energy randomization must be made, a priori (in order to infer the level of reactant excitation from the measured mean translational energy in products), and in a way which eliminates the possibility of testing for energy localization. Even granting this assumption, no quantitative estimate of a unimolecular A-factor can be extracted by comparing pumping and decay rates, because no quantitative information is available for the radiative pumping rates.

The MPD experiment reported here measures in a fairly direct way the level of excitation of reactant molecules, and then uses the quantitative information for radiative pumping rates, available from our previously reported pressure fall-off analysis, to extract an A factor. In both these respects the results are new.

A SIMPLE THEOREM

The following theorem shows the particular appropriateness of using a measurement of the distribution of total energy in reaction products to test theories of unimolecular decay:

In an ideal collisionless MPD experiment using a square laser pulse of sufficient intensity to effect complete reaction while the pulse is on, the distribution of total energy in reaction products is completely determined by the microscopic unimolecular decay rates and the radiative pumping rates between reactive states only.

Under the conditions specified in the theorem, all uncertainties associated with pumping through the low-lying discrete levels (coherent effects, bottle-necking, molecule-specific energy level details and hot band effects) play no role in determining the distribution of total energy in reaction products.

Information obtained from a product energy distribution measurement complements that obtained from the more usual MPD experiment in which the total product...
yield, produced during and after the pulse, is determined as a function of laser fluence and/or intensity. The fact that, under collisionless conditions, the total yield is essentially independent of the unimolecular decay rates and pumping rates for states above the reaction threshold was overlooked in the first claim of the applicability of RRKM theory to MPD results. Effects connected with pumping through the low-lying discrete levels are known to play a role in determining total product yield. 18

The theorem, as stated, follows from the fact that with a square pulse any molecule arriving at the first reactive level, regardless of the time it arrives there, "sees" the same laser intensity and hence has the same probability of reacting from a given total energy channel. We now present a formal proof that also establishes some results needed to interpret our experiment.

Consider the rate equations

\[ \frac{dN_i}{dt} = R_{i \to i-1} N_{i-1} - R_{i \to i+1} N_{i+1} - R_{i-1 \to i} N_i - R_{i+1 \to i} N_i - k_i N_i , \]

(1)

where \( N_i \) is the population of laser excited molecules that have absorbed \( i \) quanta from the radiation field, and have total internal energy \( E_i = i(\hbar \nu) \). The radiative coefficients \( R_{i \to i+1} \) specify the rate of absorption and stimulated emission by a molecule whose state is specified, in a coarse grained sense, by just total energy content. These coefficients are proportional to the laser intensity \( I(t) \):

\[ R_{i \to i+1} = \alpha_{i \to i+1} I(t) , \]

(2)

and in pulsed experiments should, in principle at least, be treated as time-dependent quantities. The microscopic decay constants \( k_i \) specify the rate of unimolecular decay for molecules with internal energy \( E_i \). They are identically zero for states whose energy lies below the reaction threshold: \( k_i = 0 \) if \( E_i < E_0 \). It is now generally accepted that rate equations \(1, 5, 11, 13 \) of the form given in Eq. (1) adequately describe the incoherent stepwise absorption of IR photons that occurs after the absorption of the first few photons gives the molecule sufficient energy to be in the so-called quasicontinuum, or dense manifold of internal states. The energy randomization assumption is implicit in Eq. (1). 14

Let the state \( i = m \) be the lowest lying state above the reaction threshold and define

\[ S(t) = R_{m-1 \to m} N_{m-1} - R_{m-1 \to m} N_m . \]

(3)

Then in a formal sense the reduced set of rate equations for \( i = m \), describing radiative pumping and unimolecular decay in reactive states only, can be treated as a closed set of equations with a source term \( S(t) \) appearing in the \( i = m \) equation. Let \( N_i(t, t') \) be the Green's function solution obtained by solving this reduced set of rate equations with a delta-function \( \delta(t - t') \), source term. One has

\[ N_i(t) = \int_{-\infty}^{\infty} S(t') N_i(t, t') dt' , \quad i \geq m . \]

(4)

For the yield of products \( Y_i \) formed from the total energy channel \( E_i \), one has from Eq. (1):

\[ Y_i = k_i \int_{-\infty}^{\infty} N_i(t) dt . \]

(5)

Substituting Eq. (4) and interchanging the order of integration yields

\[ Y_i = k_i \int_{-\infty}^{\infty} S(t') \int_{-\infty}^{\infty} N_i(t, t') dt' dt . \]

(6)

If in Eq. (2), \( I(t) \) is constant in time, as it is for a square pulse, then the reduced set of rate equations has constant coefficients and the Green's function has the form

\[ N_i(t, t') = N_i(t - t') . \]

(7)

In this special case the inner integral in Eq. (6) is independent of \( t' \). Thus all dependence on the source term drops out of the normalized expressions

\[ f_i = Y_i \int \sum_{i=0}^{\infty} Y_i = k_i \int_{-\infty}^{\infty} N_i(t, t' = 0) dt \]

(8)

and the theorem is proved.

It follows from Eqs. (1), (3), and (5) that the total yield is given by

\[ Y = \sum_{i=0}^{\infty} Y_i = \int_{-\infty}^{\infty} S(t) dt , \]

(9)

a result that requires no assumptions about the shape of the laser pulse. Since for polyatomics absorption is more probable than stimulated emission most molecules which arrive at the first reactive level go on to react without crossing back into a nonreactive state. As a consequence the source function is only slightly perturbed by the details of pumping through the reactive states. The comments made earlier about the insensitivity of the total yield to unimolecular decay rates and radiative pumping rates between reactive states then follows from the insensitivity of the source function to these same factors.

RESULTS AND DISCUSSION

We have used the laser excited fluorescence technique to state-selectively analyze products in the CO2 laser induced MPD 15:

\[ \text{CF}_2\text{CFCI} \rightarrow \text{CF}_2 + \text{CFCI} . \]

In this way the distribution of energy in the \( v_2 \)-bending mode of the \( \text{CF}_2 \) fragment was determined directly from level population measurements \( 0 \leq \nu_2 \leq 7 \). This distribution has an exponential form and can be adequately represented by a Boltzmann distribution with an effective vibrational temperature \( T_{\nu_2} = 1860^\circ \text{K} \). 16 Two independent measurements, via a relaxation method and a rotational contour analysis, were consistent with a Boltzmann distribution of rotational energy in the \( \text{CF}_2 \) radical. Both measurements gave the same effective rotational temperature \( T_{\nu_2} = 1550^\circ \text{K} \). 18 The same rotational contour was found for different vibrational levels \( \nu_2 = 0, 1, 5 \) indicating no correlation between rotational energy and \( \nu_2 \)-vibrational energy. Although there is no a priori theoretical reason for a Boltzmann distribution of internal energy, such distributions have been
energy in products and plotted in Fig. 1. The mean total energy in products is 7050 cm$^{-1}$. Besides the assumptions detailed in Ref. 16, two additional assumptions are made in order to arrive at the plotted distribution. It is assumed that the rotational energy distribution in CFCI is the same as that measured in CF$_2$, which must be approximately correct when one considers that angular momentum is conserved when these two structurely similar fragments separate. It is also assumed that the energies of the CF$_2$ and CFCI fragments are uncorrelated. This latter assumption does not affect the mean of the distribution.

Reliable estimates of radiative pumping rates are available for CF$_2$CFCI. These come from our previously reported$^7$ analysis of the time resolved rates of MPD determined as a function of laser intensity and added inert buffer gas pressure. Experimental results and theoretical curves are shown in Fig. 2. The inert buffer gas Ar present in large excess, remains cold during the experiment. The fall-off in the rate, observed for $P_A > 100$ Torr, results from $V-T$ deactivation by collision between excited CF$_2$CFCI and cold Ar molecules. The competition, laser excitation with collisional deactivation, provides a sensitive test of the theoretical expressions for radiative pumping rates that were used in this analysis. These expressions are derived from the single quantum exchange model$^{15}$ for homogeneous level broadening:

$$\text{Width} = 2\pi \frac{\hbar^2}{\omega} \rho^{\text{ex}}(E)$$.  \hspace{1cm} (10)

Here $\rho^{\text{ex}}(E)$ is the so-called single quantum exchange density of states. At low pressures $^1(P_A < 100$ Torr) one observes, cf. Fig. 2, experimental rates that consis-
The full density of states for vibrational degrees of freedom of the absorbing molecule
plays an important role in determining the calculated mean total energy in products should agree with the measured value of 7050 cm$^{-1}$. The following points summarize the results:

(i) The calculated fit for pressure and intensity results is (when the constraint on total energy in products is ignored) totally insensitive to $A$, large variations in $A$ being compensated by quite small variations in $\delta$.

(ii) Only the fit of pressure and intensity results is required to uniquely determine $\Delta E$. The value found $\Delta E = 2.7$ kcal/mole lies within the range $1 < \Delta E < 3$ kcal/mole expected on the basis of chemical activation studies.

(iii) The calculated mean total energy in products 7050 cm$^{-1}$ is quite sensitive to $A(\approx 10^{16}$ sec$^{-1}$ gives a mean of 8470 cm$^{-1}$), and relatively insensitive to small uncertainties in $\delta$. The parameter $\Delta E$ does not enter into this calculation. The value found, $A = 3.2 \times 10^{16}$ sec$^{-1}$ is close to our previous estimate, $A = 1 \times 10^{16}$ sec$^{-1}$.

This value, $A \approx 3 \times 10^{16}$ sec$^{-1}$, is the first to be determined from MPD measurements. Since it lies within the range, $1 \times 10^{15} < A < 1 \times 10^{17}$ sec$^{-1}$ expected for this type of reaction, we have here a quantitative check of the applicability to MPD of a statistical theory of unimolecular decay.

Using Eq. (9), we have also calculated the probability distribution for total energy in products. Results are shown in Fig. 1. That the theoretical curve is somewhat narrower than the experimental is most likely due to the assumption of a square pulse in the theoretical calculation and/or the assumption of no correlation between different degrees of freedom made in determining the experimental curve. Approximate calculations indicate that correlation in the energy of the fragments cannot give rise to a significant narrowing in the experimental curve. With a pulse that is not flat, different molecules see different laser intensities as they are being pumped between reactive states. As a result more molecules react with energy at the low and high energy tails of the distribution when compared to the flat pulse case. However, this should not result in a significant shift in the mean energy.
CONCLUDING REMARKS

As a test of either RRK of RRKM theory by MPD, there are two unique advantages to the method reported on in this paper. (i) Because the distribution of total energy in reaction products is measured, the level of excitation above threshold in reactant molecules is known directly. In the work of Lee and co-workers, the level of excitation above threshold is inferred (by a calculation which assumes energy randomization for the distribution of energy between translational and internal degrees of freedom) from a measurement of the mean translational energy in the products. (ii) Because reliable estimates of the radiative pumping rates are known from a separate study of MPD rates as a function of laser intensity and inert buffer gas pressure, the test is quantitative.

Since at any given reactive level there is a competition between radiative pumping and unimolecular decay one expects the maximum decay from that level for which the rates of these two processes are about equal. In our calculation equality occurs at 8 laser quanta above the activation threshold. Here the RRK decay rate is $1.57 \times 10^{10} \text{sec}^{-1}$ and the radiative pumping rate for an up transition is $1.52 \times 10^{10} \text{sec}^{-1}$. At nine quanta above threshold the decay rate is already twice the pumping rate. This order of magnitude argument is in remarkably good agreement with the complete calculation (cf. Fig. 1) which shows maximum decay occurring for 7 excess quanta. An approximate RRKM calculation of the microscopic decay rates (using a transition state model constrained to give $A = 3 \times 10^{16} \text{sec}^{-1}$) shows equality in decay and radiative pumping rates occurring at about 8.5 excess quanta. Hence, the use of RRKM rates instead of RRK rates would have no substantial effect on the results.

Suppose energy were not randomized? Then the microscopic decay rates might be drastically changed. For example, if one takes $s = 6$ in Eq. (11), i.e., limiting the energy randomization to 6 of the 12 vibrational degrees of freedom, and equates radiative and decay rates at 6 excess quanta, one finds $A = 2.3 \times 10^{13}$. This value is well outside the accepted range $10^{12} \leq A \leq 10^{17}$ for this type of reaction. Our results therefore support the conclusion that in this experiment, energy is fairly well randomized before reaction can occur.

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25. J. L. Lyman, G. P. Quigley, and O. P. Judd [to be published in Multiple-Photon Excitation and Dissociation of Polyatomic Molecules, edited by C. Cantrell (Springer-Verlag, Heidelberg, West Germany)].
30. This conclusion would be invalidated if our pumping rates (determined as they are at high pressures where collisional processes destroy energy localization) were significantly lower than the zero pressure pumping rates required for the energy distribution calculation. However, if energy localization were to affect the pumping rates one would expect randomization by collision to increase, not decrease the pumping rates. (It's easier to pump a big molecule than a small one.)