CLASSICAL TRAJECTORY STUDY OF INFRARED MULTIPHOTON PHOTODISSOCIATION

D.W. NOID, M.L. KOSZYKOWSKI, R.A. MARCUS and J.D. McDONALD
Department of Chemistry, University of Illinois, Urbana, Illinois, USA

Received 28 July 1977

Classical trajectories on a realistic model potential energy surface (approximating one dissociation channel of CD_3Cl) driven by an external force have been used to model infrared multiphoton dissociation. This model predicts a reasonable energy density threshold behavior, and generally (except at extremely high power densities) shows random (RRKM-like) behavior of the highly excited molecules, although non-random effects are evident immediately after the field is turned on.

1. Introduction

In the past few years a considerable body of experimental data has been collected on the phenomenon of multiphoton infrared dissociation *, and several theoretical models [12–15] have been proposed which, qualitatively, account for most aspects of the observed data. The published explanations and calculations are all based on simplified models. It would be very appealing to have exact calculations on a model based on a realistic potential energy surface for some reaction. This appears to be a particularly challenging task for at low molecular excitations the interaction of light and matter has been traditionally treated quantum mechanically, while at high molecular energies quantum mechanical treatments are impossible (due to the great number of states) and indeed classical mechanics has been shown to be nearly exact at these high state densities. Even at low energies classical mechanics has satisfactorily (if not exactly) explained most *collision* phenomena of molecules which are classically allowed, since quantum interferences are unobservable due to averaging over a distribution of initial states [16]. Because absorption and stimulated emission of radiation are classically allowed we might hope that the phenomenology of multiphoton dissociation would be correctly described by classical mechanics and electrodynamics, as the averaging over random photon absorption and emission times should hide quantum beat effects. (This assumes that the whole photodissociation process occurs on a time scale short compared to *spontaneous* emission which *is* inherently quantum. This condition is met by most of the experiments.)

We have performed classical calculations upon a molecular model whose behavior has been previously studied in detail [17] **. This model consists of a force field which models the C–Cl dissociation channel of CD_3Cl. The other possible reaction pathways are closed in this model. The interaction with the radiation field is included in the form of a force on the C–Cl bond:

$$F = \mathcal{E}(t) \cdot D'(r_{C-Cl}),$$

where

$$\mathcal{E}(t) = [I(t)]^{1/2} \hat{k} \cos \omega t;$$

k is a space-fixed unit vector, and $D(r_{C-Cl})$ is the dipole moment function for the molecule:

$$D'(r_{C-Cl}) = \frac{\mathrm{d}D(r_{C-Cl})}{\mathrm{d}r_{C-Cl}} = \frac{r_{C-Cl}}{|r_{C-Cl}| + 0.064|r_{C-Cl}|^4},$$

---

* See, for example, papers on the subject presented in ref. [1], and references therein; see also refs. [2–11].

** The present study used the variant of this potential surface with C–Cl stretching parameters 3.00 and 2.60 rather than 1.75 and 3.4042. The behavior of isolated CD_3 is unaffected. The method of analysis of each trajectory used proceeds through spectra, calculated for each zero order normal mode by a correlation function procedure.

with distances in Å, electric field in V/Å and force in eV/Å. Note that only the C–Cl bond contributes to the dipole function so that separated CD_3 does not interact with the field. Also $I(t)$ is the intensity of the laser field as a function of time.

We have made a systematic study of the dependence of the rate of deposition of energy into different modes of CD_3Cl and of the rate of dissociation versus the power and frequency of the laser field in the vicinity of the 1361 cm^{-1} (0.4082 tHz) vibration of the model CD_3Cl molecule (mode 3 of ref. [17]). This vibration represents essentially the C atom moving along the symmetry axis of the molecule with the Cl and D's remaining almost fixed. The $I(t)$ function was

$$I(t) = I_0 \sin^2(\pi t/1600)$$

for times $0 < t < 1600$, the units for t being 10^{-14} s. Thus, the pulse lasts 16 ps. The value of I_0 was varied as was ω. Batches of 18 trajectories were run for each I_0, ω pair. The trajectories were started with 0.01 eV, in each normal mode, with random phases and zero angular momentum. The energy in each zero order normal mode was calculated over intervals of 2.5 ps each for trajectory using the method described previously [17,18]. Batches were run at a power density (at the peak of the pulse) of 8.50 tW/cm^2 * and frequencies of 0.36, 0.37, 0.38, 0.39, 0.40 and 0.41 Hz and at peak power densities of 13.27 and 4.78 tW/cm^2 at 0.38 tHz. These three peak power densities correspond to pulse energy densities of 38.2, 68.0, and 106.2 J/cm^2.

Two more batches of trajectories each were run at a frequency of 39 tHz and at lower power densities (rising from zero to the peak value in 1.0 ps and thereafter being constant) of 1.19 tW/cm^2 and 0.132 tW/cm^2. These trajectories were run only as long as necessary to dissociate the CD_3Cl molecule. They were started with the molecules having quantum zero point energies in each mode, random phases, and zero angular momentum. Only the internal energy versus time and time of dissociation were tabulated for these trajectories. The small number of trajectories in each batch were due to the large amount of computer time needed.

Four trajectories were run to test the effect of having two laser fields at once. Two trajectories were run at a power density of 8.5 tW/cm^2 and 75 tHz and two with two fields, one at 8.5 tW/cm^2 and 75 tHz and one at 0.132 tW/cm^2 and 39 tHz. These trajectories were also started with quantum zero point energies and random phase in each mode, and zero angular momentum.

Table 1

Fraction of molecules dissociating f_{diss}, fraction dissociating during laser pulse f^0_{diss}, average energy absorbed per molecule E_{abs} and average translational energy of products E_{trans} versus initial frequency ω and power density E for batches of trajectories exposed to 16 ps laser pulses

ω (tHz)	E (J/cm^2)	f_{diss}	f^0_{diss}	E_{abs} (eV)	E_{trans} (eV)
36	68	0	0	0.2	
37	68	0	0	0.2	
38	38	0.06	0	1.3	
38	68	0.8	0.6	4.0	0.2
38	106	1.0	0.8	4.5	0.2
39	68	0	0	1.3	
40	68	0	0	0.8	
41	68	0	0	0.5	

2. Results

The major results of this study are given in figs. 1–4 and table 1. Table 1 lists each of the batches with 16 ps pulse lengths giving the frequency of excitation ω,

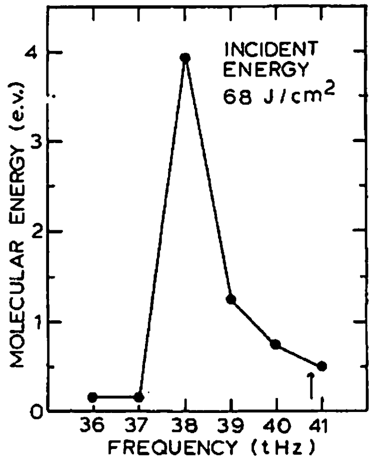

Fig. 1. Average energy absorbed per molecule for trajectories with 16 ps incident laser pulses at 68 J/cm^2 versus laser frequency ω.

---

* A terawatt is 10^{12} W; a terahertz (10^{12} Hz) corresponds to 33.33 cm^{-1}.

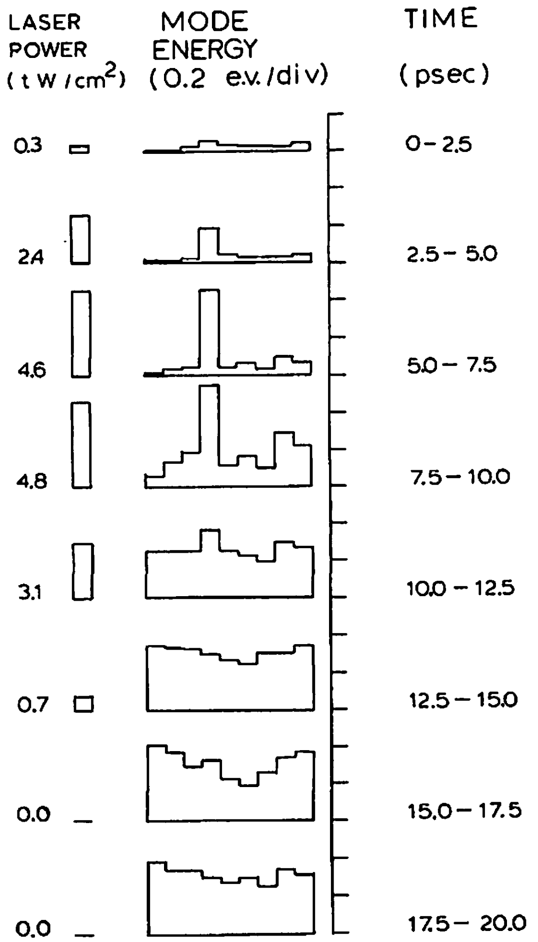

Fig. 2. The growth in energy in each of the nine normal modes of CD_3Cl versus time, averaged over 2.5 ps intervals. The average laser power density is shown for each time interval in the left column. The center group shows the energy in each of the nine modes versus time (leftmost is highest normal mode frequency, rightmost is lowest, and forth highest mode is being pumped). Due to the small number of trajectories being averaged the variation due to random error is large; the lowest two panels show no variation outside this statistical error.

the incident energy density E, the fraction of molecules which dissociated f_{diss}, the fraction of molecules which dissociated *during* the laser pulse f^0_{diss}, the average amount of energy absorbed per molecule, E_{abs}, and average relative translational energy of the product molecules, E_{trans}.

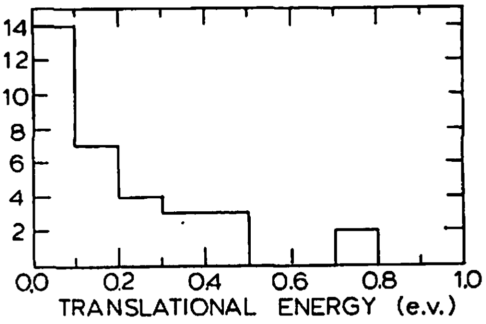

Fig. 3. Product translational energy distribution for batch of trajectories exposed to 16 ps pulse of frequency 38 tHz and incident energy 106 J/cm².

It was previously shown [4] that the amount of vibrational energy in the product CD_3 molecules produced in this study is sufficient to allow randomization among all the vibrational degrees of freedom. Fig. 1 illustrates the effect of varying the laser frequency on the energy deposition in the molecules. The variation in energy deposition for different molecules in a batch is almost as wide as the averages. Fig. 2 shows the growth in energy in each of the nine normal modes of the CD_3Cl molecule for various time intervals for the batch $E = 38$ J/cm², $\omega = 38$ tHz. The incident laser power during the successive time intervals is also shown. The shape of the translational energy distribution of products for the batch at $E = 106$ J/cm² and $\omega = 38$ tHz (fig. 3) follows the shape expected of a statistical (RRKM or phase space) distribution within the considerable (±50%) random error arising from the limited (40) trajectories used.

The two batches run at constant powers of 1.19 tW/cm² and 0.132 tW/cm² were used to find the threshold energy density at realistic power levels. For the 0.132 tW/cm² batch the dissociation times for individual trajectories varied from 278 to 491 ps (incident energy density from 42 to 68 J/cm²) with the average incident energy density at dissociation being 55 J/cm². The batch at 1.19 tW/cm² dissociated at times between 41 and 132 ps (51 to 166 J/cm²) and averaged an incident power of 90 J/cm². Fig. 4 gives the internal energy of the molecule versus time for the trajectory at 0.132 tW/cm² which dissociated most rapidly. All the other trajectories in these batches look qualitatively similar.

The two trajectories at 8.5 tW/cm² and 75 tHZ did not show any net absorption of energy over 100 ps, because they are far off resonance; only fluctuations of ±0.05 eV were observed. The two two-field (75 tHz, 39 tHz) trajectories did dissociate, one at 38 ps and one at 84 ps.

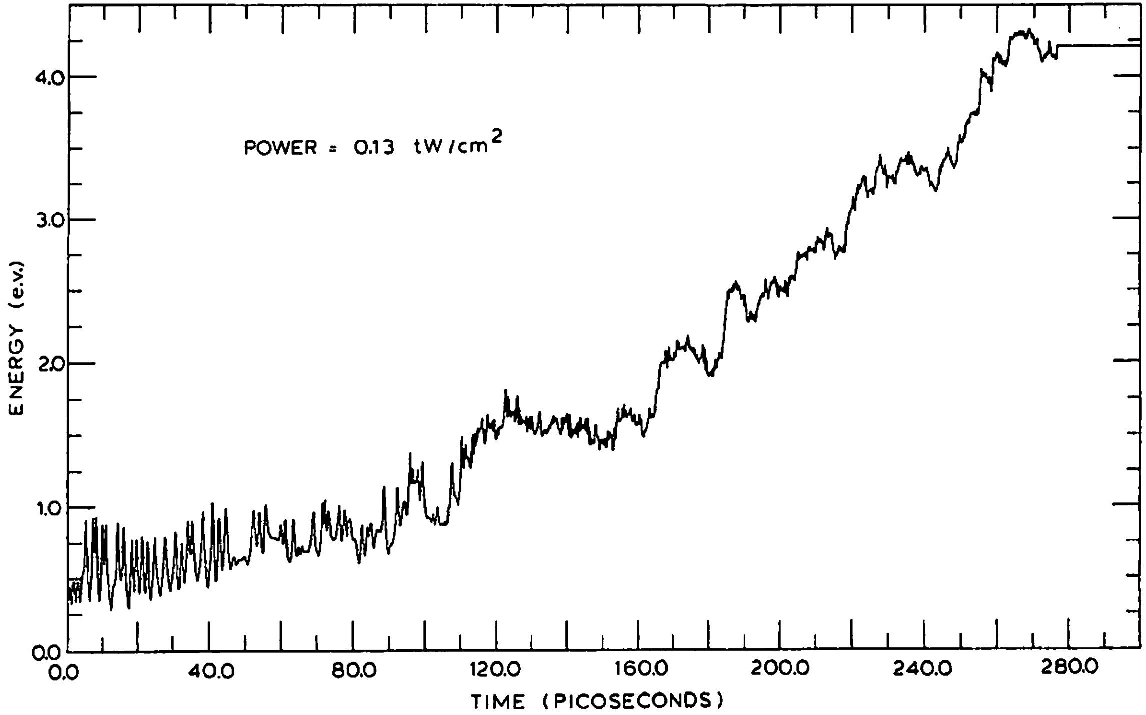

Fig. 4. Internal energy of a single molecule exposed to laser field at ω = 39 tHz and a constant power density of 0.132 tW/cm^2. The horizontal line beginning at 278 ps represents the dissociated products.

We may summarize our results as follows:

(1) At the power densities of 1.19 tW/cm^2 and 0.132 tW/cm^2, dissociation began only when the incident energy densities reached approximately the same value, 40 J/cm^2. Thus there is an energy density threshold for dissociation rather than a power density threshold, in agreement with the relevant experiments of Black et al. [10] and Coggiola et al. [11]. Since we have observed so few trajectories, a rare atypical trajectory could dissociate at somewhat lower energy densities. Because experimentalists typically see dissociation at much lower probabilities (0.01%) than our ≈10% threshold, our results are not directly comparable to experimental thresholds. Due to cost considerations it is also not feasible to explore the dissociation yield versus energy flux behavior.

(2) The long individual trajectories show an internal energy (about 1.5 eV) below which energy flows between the molecule and the field in a rather regular manner, indicating "beats" between the molecular motion and the field oscillations (fig. 4). At these low energies our earlier studies have shown that intramolecular energy randomization occurs moderately slowly, over perhaps 10^{-11} s. At higher energies (total molecular energy >1.5 eV above classical zero) these oscillations disappear, since the intramolecular energy randomization occurs faster than their period (in about 1 to 2 ps).

(3) For a given pulse length at the most effective laser frequency ω = 38 tHz) the dissociation yield is a steeply rising function of power (f_{diss}) in table 1, rising from 6% to 80% as one raises the power E by about 1.7 times.

(4) The amount of energy deposited in the average molecule E_{abs} in table 1 and fig. 1 for a constant pulse power and shape, is a steeply peaked function of the laser frequency, and the peak frequency is *lower* than the zero point frequency of the pumped normal mode (by roughly 7% for the conditions in fig. 1).

This large frequency difference is due to the very high laser power. At lower power levels the shift is less than 7%, but we have not attempted to accurately locate the peak at lower power levels, for reasons of cost.

(5) At high powers the internal energy distribution of the molecule *during* the first part of the pulse is nonrandom (fig. 2, where the pulse time is 16 ps), the pumped mode being more excited than the other modes.

After the pulse the internal energy of highly excited (4.2 eV internal energy) but nondissociated molecules randomized completely in less than 3 ps. (Because of the small number of trajectories used in fig. 2 the relative standard deviation in each value is approximately ±25%.) At lower powers we do not have enough data to assess this effect.

(6) For this particular potential energy surface the product (dissociated) molecules appear to have roughly random internal and translational energy.

(7) Two laser pulses applied simultaneously, a weak one on resonance and a strong one far from any resonance, can cause dissociation much more rapidly than either alone.

3. Discussion

The remarkable feature of this study is that a purely classical procedure, based on a realistic potential surface, qualitatively (and as far as can be expected for a model not specifically designed for the purpose, quantitatively) explains principal features of the high power infrared laser dissociation phenomenon. One predicts, thereby, that at the power levels presently employed the internal energy of highly excited (but not yet dissociated) molecules will be randomly distributed among vibrational degrees of freedom (or, in an alternate view bonds), and RRKM theory should accurately predict product yields. At very high powers (such as our 16 ps pulses) the laser can pump energy into one normal mode faster than intramolecular relaxation can spread it out and it is expected that non-random (non-RRKM) events *may* occur. We also predict (based on our previous work) that for some molecules even at low power levels, product energy distributions may not be random, bedause of exit channel effects. (For example, dissociation of the molecule $ClCH_2CH_2CH_3$ should produce as a principal product HCl in an *inverted* vibrational state distribution *.)

---

* Based on analogy to similar experiments performed by chemical activation. See ref. [19].

Acknowledgement

This research was supported by the Graduate Research Board of the University of Illinois.

References

[1] A. Mooradian, T. Jaeger and P. Stokseth, eds., Tunable lasers and applications (Springer, Berlin, 1976).
[2] V.S. Letokhov and C.B. Moore, Soviet J. Quantum Electron. 3 (1976) 259.
[3] R.V. Ambartzumian, V.S. Letokhov, E.A. Ryabov and N.V. Chekalin, JTEP Letters 20 (1974) 273.
[4] J.L. Lyman, R.J. Jensen, J. Rink, C.P. Robinson and S.D. Rockwood, Appl. Phys. Letters 27 (1975) 87.
[5] J.L. Lyman and S.D. Rockwood, J. Appl. Phys. 47 (1975) 595.
[6] R.V. Ambartzumian, Yu.A. Gorokhov, V.S. Letokhov and G.N. Makarov, JETP Letters 21 (1975) 171; 22 (1975) 43.
[7] R.V. Ambartzumian, Yu.A. Gorokhov, V.S. Letokhov and A.A. Puretskii, JETP Letters 32 (1975) 177.
[8] S.M. Freund and J.J. Ritter, Chem. Phys. Letters 32 (1975) 255.
[9] G. Hancock, J.D. Campbell and K.H. Welge, Opt. Commun. 16 (1976) 177.
[10] J.G. Black, E. Yablonovitch and N. Bloembergen, to be published.
[11] M.J. Coggiola, P.A. Schulz, Y.T. Lee and Y.R. Shen, Phys. Rev. Letters 38 (1977) 17.
[12] N. Bloembergen, Opt. Commun. 15 (1975) 416.
[13] D.M. Larsen and N. Bloembergen, Opt. Commun. 17 (1976) 254.
[14] R.V. Ambartzumian, Yu.A. Gorokhov, V.S. Letokhov, G.N. Makarov and A.A. Puretzkii, JETP Letters 23 (9176) 22.
[15] S. Mukamel and J. Jortner, Chem. Phys. Letters 40 (1976) 150.
[16] W.H. Miller, Accounts Chem. Res. 4 (1971) 161.
[17] J.D. McDonald and R.A. Marcus, J. Chem. Phys. 65 (1976) 2180.
[18] D.W. Noid, M.L. Koszykowski and R.A. Marcus, J. Chem. Phys. (July 15, 1977), to be published.
[19] J.T. Gleaves and J.D. McDonald, J. Chem. Phys. 62 (9175) 1582.