

# Classical trajectory studies of the photodissociation reaction of *sym*-triazine

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Classical trajectory simulations were performed for the photodissociation of *sym*-triazine on an interpolated potential energy surface, for energies equivalent to 193, 248, 266, 285, and 295 nm light. Initial conditions were chosen using microcanonical normal mode sampling. The calculated average translational and rotational energies of the HCN products were in good agreement with some experimental results. The shapes of the product translational energy distributions are also in good agreement with experiment for low energy light, but a little narrower than the experimental distributions at high energies.

## I. Introduction

The photodissociation reaction of *sym*-triazine has been studied using various experimental<sup>1–5</sup> and theoretical<sup>6–10</sup> methods. In their early experimental study on this reaction, Ondrey and Bersohn<sup>4</sup> measured time-of-flight (TOF) spectra after excitation by laser pulses of 193 and 248 nm. The most extensive study of the product translational energy distributions were measured by Gejo *et al.*<sup>3</sup> by “photofragment translational spectroscopy” (also a TOF method) with 295, 285, 275, 248, and 193 nm lasers. Goates *et al.*<sup>5</sup> studied the reaction by observing infrared emission from the product bending and C–H stretching modes. Park<sup>2</sup> measured the translational and rotational energies of the HCN products (from photodissociation with 266 nm light) from Doppler broadening and population analysis of rotational excitation by a diode laser. Kim and Kim<sup>1</sup> studied the reaction using a coherent antistokes Raman scattering technique to measure the rotational energy of the products from photodissociation at 248 and 193 nm energies.

When *sym*-triazine is excited by ultraviolet light, it can undergo a  $\pi^* \leftarrow n$  transition, which puts the system in an <sup>1</sup>E state, or a  $\pi^* \leftarrow \pi$  transition which excites the system into an <sup>1</sup>A<sub>1</sub> state. In either case, the excited molecule proceeds *via* rapid internal conversion to the ground state with excess energy, so that dissociation ensues. This high energy dissociation can be studied using classical trajectories.<sup>9,11</sup>

In the traditional approach, a classical trajectory simulation is based on an analytical potential energy surface (PES), which may be constructed in part from quantum chemistry calculations. However, this method requires fitting of numerical data to a complex functional form with many adjustable parameters. Recent developments in computing capability make a direct dynamics method<sup>12</sup> feasible for moderate size systems. However, it is still too expensive to perform direct dynamics classical trajectories with high level electronic structure theory for larger systems. An alternative way to overcome this problem is to use an interpolated PES.<sup>13</sup> This method had been successfully applied to various systems, and is described in detail elsewhere.<sup>13</sup>

The interpolated PES approach was recently used for a simulation of the title reaction following 295 nm laser excitation.<sup>9</sup> This study showed that the observed energy distribution of the dissociation products is consistent with a concerted

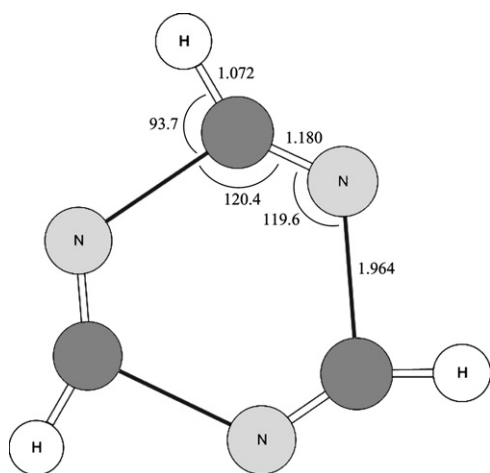
mechanism which produces three HCN molecules in a single step. The agreement between the calculated and observed<sup>3</sup> product energy distributions also suggests that the interpolated PES is sufficiently accurate.

However, this classical simulation was limited in a number of ways. Only one excitation energy was considered, although experimental data is available over a range of energy. Each trajectory was initiated in the region of the saddle point for the concerted dissociation. The trajectory initial conditions were sampled using an efficient microcanonical sampling (EMS) method,<sup>14</sup> which does not simulate the quantization of bound vibrational modes near the saddle point. This paper reports classical trajectory simulations which use microcanonical normal mode sampling in the saddle point region.<sup>15</sup> The apparent effect of this modification of the original approach is to produce initial conditions that are more closely confined to the saddle point region, even at much higher energy. The consequences of this sampling method are examined here where we report theoretical and observed product distributions over a range of energies. This provides a more thorough test of the interpolated PES and classical methodology. The variation in product energy distributions reported from experiments is also discussed.

In section II, the computational methods are described. Results of calculations at the energies of 193, 248, 266, 285, and 295 nm laser excitations are presented in section III. Conclusions are contained in section IV.

## II. Methods

The calculations reported here employ the same interpolated PES constructed previously, based on the BLYP/6-31G\*\* level of theory.<sup>9</sup> Comparison of this level of theory with other theoretical and experimental results for *sym*-triazine has been considered elsewhere.<sup>7,9</sup> A detailed survey of density functional theory (DFT) and *ab initio* results was reported by Pai *et al.*<sup>7</sup> (see Table 4 of ref. 7). The lowest energy pathway to photodissociation was found to be *via* a concerted mechanism with a threefold symmetric saddle point, as illustrated in Fig. 1. A two step pathway, involving formation of H<sub>2</sub>C<sub>2</sub>N<sub>2</sub> + HCN, was also found, though at higher energy. We note that the zero-point-energy-corrected energy difference between the



**Fig. 1** Schematic representation of the saddle point on the PES for the concerted dissociation of *sym*-triazine to three HCN products. The bond lengths are shown in ångströms and the bond angles are shown in degrees.

saddle point of Fig. 1 and the reactant is  $74.8 \text{ kcal mol}^{-1}$  for BLYP/6-31G\*\* compared to the most reliable available estimate of  $81.2 \text{ kcal mol}^{-1}$  at the QCISD(T)//MP2/cc-pVTZ level. The energy difference between the product (3 HCN) and reactant is  $42.1 \text{ kcal mol}^{-1}$  at BLYP/6-31G\*\* and  $32.0 \text{ kcal mol}^{-1}$  at QCISD(T)/cc-pVTZ, where the experimental value is  $43.2 \text{ kcal mol}^{-1}$ .

The PES was constructed from calculations of the electronic energy, and first and second derivatives of the energy, at molecular configurations which were encountered in trajectory simulations. These trajectories were initiated in the region of the saddle point geometry (Fig. 1), and were restricted to an energy corresponding to 266 nm excitation of the molecule. Based on an earlier study of this type of interpolated PES,<sup>16</sup> it might be expected that simulations at much higher energies would be less reliably accurate.

In this study, as previously,<sup>9</sup> it is assumed that the photo-excited molecule only dissociates by passing through a transition state (TS) which is located at the saddle point of Fig. 1. The total energy of the molecule at the TS is fixed as before as follows.<sup>9</sup> The most reliable available estimate for the energy difference (including zero point energies) between the TS and the reactant is the QCISD(T)//MP2/cc-pVTZ value of  $81.2 \text{ kcal mol}^{-1}$ .<sup>6</sup> The corresponding BLYP/6-31G\*\* value is lower at  $78.4 \text{ kcal mol}^{-1}$ . To correct for this underestimation of the TS energy, the energy available to the molecule on the BLYP/6-31G\*\* surface at the TS is taken to be the photon energy minus the more reliable value of  $81.2 \text{ kcal mol}^{-1}$ . For 266 nm light ( $107.4 \text{ kcal mol}^{-1}$ ), this calculation gives an energy  $26.2 \text{ kcal mol}^{-1}$  above the zero-point-corrected BLYP/6-31G\*\* TS and  $59.0 \text{ kcal mol}^{-1}$  above the estimated (BLYP/6-31G\*\*) ground state of the three HCN products. The later value is  $3.6 \text{ kcal mol}^{-1}$  less than the experimental value.<sup>2</sup> That is, the total energy available to the products for the simulated dissociation on the BLYP/6-31G\*\* PES is fortunately just  $3.6 \text{ kcal mol}^{-1}$  less than the experimental value.

The vibrational motion around the TS is described in the harmonic approximation. The reaction coordinate is taken to be a displacement in the direction of the vibrational eigenvector which has an imaginary frequency. The available energy, for each photon energy, was distributed between the vibrations and motion along the reaction coordinate by microcanonical sampling of classical harmonic oscillators.<sup>15</sup> No energy was allocated to overall rotation of the molecule. The associated Monte Carlo sampling produces random molecular configurations and atomic momenta consistent with this energy distribution. The microcanonical normal mode sampling appears to

generate initial molecular configurations that are within the region of validity of the interpolated PES. In contrast, the EMS method, at higher energy, leads to trajectories which do not conserve energy as the molecular configurations fall outside the region where the interpolated PES is smoothly varying.

Five hundred sets of such initial coordinates and momenta for the atoms were generated for each photon energy, and each classical trajectory was integrated until the molecule either dissociated or moved into the reactant channel. Movement into the reactant channel was measured by a change in the local internal coordinate<sup>17</sup> which corresponds to negative curvature of the potential energy surface at the saddle point. Because of the random sampling of momenta, about half of the trajectories went to the reactant region. The initial atomic momenta for each trajectory were reversed, and the trajectories were integrated to dissociation or to the reactant. The results of all 1000 trajectories were then collected for analysis.

The total energies of each set of initial conditions showed some variation across the set, of the order of  $1.5\text{--}3.7 \text{ kcal mol}^{-1}$ . This is due to the harmonic oscillator approximation used in this sampling method and to interpolation error. This uncertainty in the initial total energy limits the precision with which the final product energy distributions can be described. The classical trajectories were integrated with a time step of about  $2 \times 10^{-17} \text{ s}$ . A small number (1–5 in 1000) of “nonconserving” trajectories failed to conserve the total energy to within a tolerance of about  $10^{-3}$  of the available energy. This failure is most probably due to inaccuracy in the gradient of the interpolated PES, and indicates a small additional uncertainty in the results obtained.

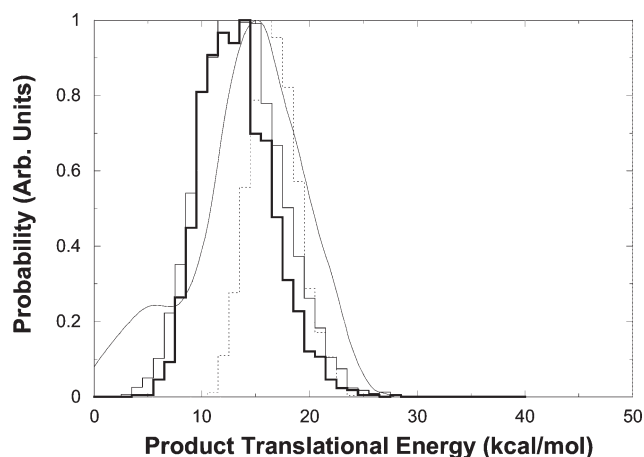
### III. Results and discussion

We have calculated classical trajectories for photodissociation at the energies of 193, 248, 266, 285, and 295 nm photons. The numbers of reactive and “nonconserving” trajectories are given in Table 1. The number of reactive trajectories was higher than 50% of the total, which might be described as a barrier recrossing effect, since some trajectories lead to products with and without reversal of the initial momenta.<sup>18</sup> No attempt was made to vary the location or orientation of the transition state dividing surface in order to minimize this effect.

The translational energy distribution of HCN products from photodissociation at 295 nm is shown in Fig. 2. The result of the present study which uses microcanonical normal mode sampling is in agreement with the previous result obtained using the EMS method.<sup>9</sup> This might suggest that the normal mode approximation at the TS does not significantly affect the trajectory results, at least at the lowest energy reported. The good agreement with experimental data suggests that the available energy is randomized in all of the vibrational modes, as in the assumption of statistical theory. The dotted line in Fig. 2 is the result of trajectories for which all the vibrational modes were in their ground states at the TS, so that all the available energy was in translational energy along the reaction coordinate. This result is presented for comparison only, to

**Table 1** The results of 1000 trajectories which simulate *sym*-triazine photo-excited with various photon wavelengths

Energy/nm	Number of reactive trajectories	Number of nonconserving trajectories
295	592	0
285	600	1
266	607	1
248	625	2
193	639	5



**Fig. 2** The experimental total translational energy distribution for the three HCN products from the simulation of photodissociation by 295 nm light is compared with calculated results. The smooth solid line is the experimental data of Gejo *et al.*<sup>3</sup> The result of this study using microcanonical normal mode sampling is the thick solid line. A previous result using the efficient microcanonical sampling method is shown as a thin solid line. The result of fixed normal mode sampling with ground state vibrational energy is indicated by the dotted line.

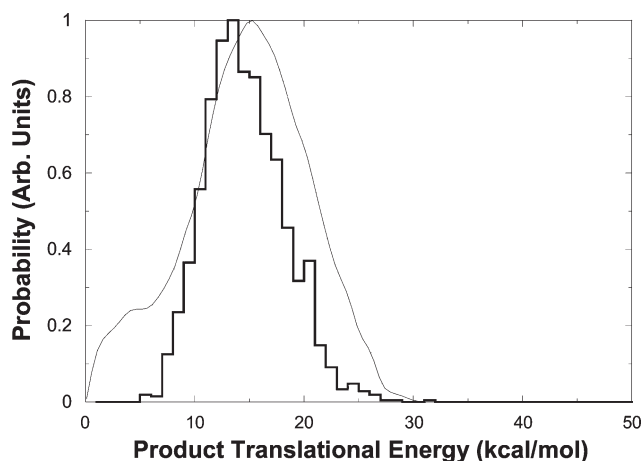
indicate the consequence of this extreme initial condition. This limit produces a relatively narrow translational energy distribution with a peak at higher energy than is obtained from other initial energy distributions.

The average translational and rotational product energies are presented and compared with experimental results in Table 2 for a range of excitation energies. There are considerable differences between the reported results of different experiments. The product translational energies obtained by Ondrey and Bersohn<sup>4</sup> are very low compared with the two comparable experimental results from Gejo *et al.*<sup>3</sup> Park<sup>2</sup> inferred an average translational energy of 84% of the available energy for photodissociation at 266 nm. Although no data is available from Gejo *et al.* at this frequency, one might reasonably predict from their results a somewhat lower value of about 70%. The rotational energy reported by Park<sup>2</sup> for 266 nm light was 15%, which is qualitatively different from the low values reported in other experiments<sup>1</sup> at higher energy. Goates *et al.* also observed very little rotational excitation at 193 nm.<sup>5</sup> High vibrational excitation was observed by Kim and Kim<sup>1</sup> and Goates *et al.*,<sup>5</sup> while Park<sup>2</sup> reported very little excitation in vibration. The experimental results are, therefore, somewhat conflicting, but suggest that rotational excitation is low, at least at high photon energies, and that product translational energy is generally high, in the 60–80% range. The translational and rotational energies calculated here using microcanonical normal mode sampling are in reasonable agreement with these basic trends. Indeed, the calculated translational energies are in very good agreement with the results of Gejo *et al.*, albeit somewhat lower at high photon energy.

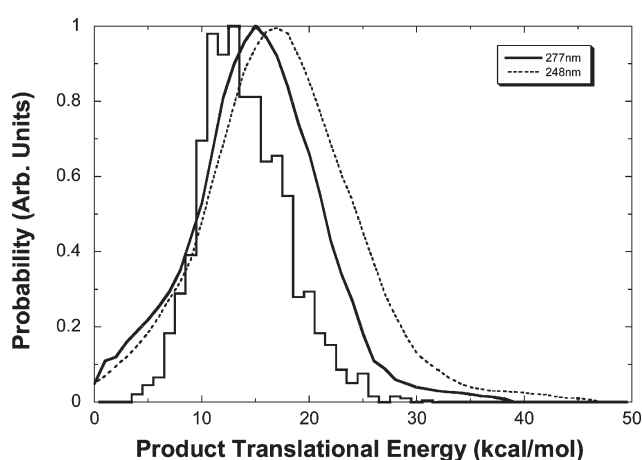
Figs. 3 to 6 present the translational energy distributions for the other energies studied. The locations of the peaks are a bit

**Table 2** Total average translational and rotational (in parentheses) energies of the three HCN products as a percentage of the total available energy

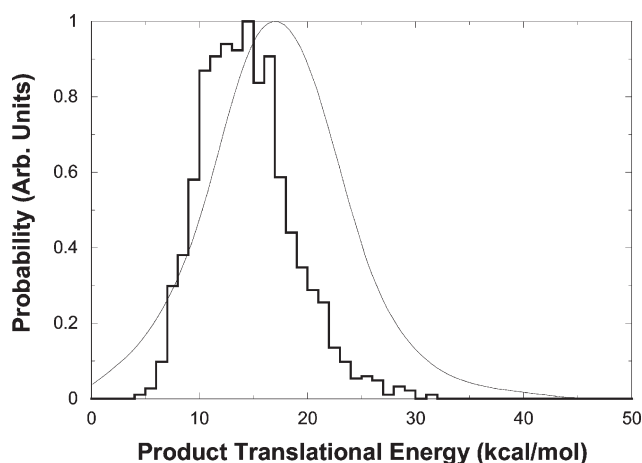
Wavelength	This study	Ref. 1	Ref. 3	Ref. 4	Ref. 2
295	74.3 (6.2)		72.6		
285	70.4 (6.5)		72.2		
275			70.9		
266	64.8 (7.0)				84.0 (15.0)
248	59.1 (7.1)	(2.8)	69	39.5	
193	45.0 (7.9)	(2.5)	54.5	5.5	



**Fig. 3** As in Fig. 2, but for photodissociation by 285 nm light. The smooth solid line is the experimental data of Gejo *et al.*<sup>3</sup> The result of this study using microcanonical normal mode sampling is the thick solid line.

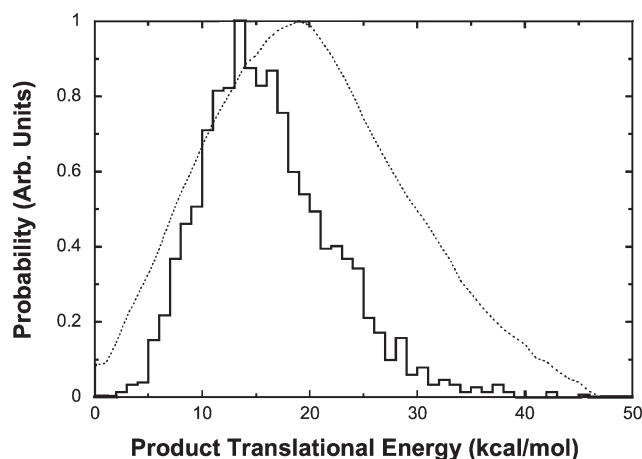


**Fig. 4** As in Fig. 2, but for photodissociation by 266 nm light. The experimental distributions shown are data from Gejo *et al.*<sup>3</sup> for 248 and 275 nm light.



**Fig. 5** As in Fig. 2, but for photodissociation by 248 nm light. The smooth solid line is the experimental data of Gejo *et al.*<sup>3</sup> The result of this study using microcanonical normal mode sampling is the thick solid line.





**Fig. 6** As in Fig. 2, but for photodissociation by 193 nm light. The smooth solid line is the experimental data of Gejo *et al.*<sup>3</sup> The result of this study using microcanonical normal mode sampling is the thick solid line.

lower than the experimental ones. One reason for this could be due to the fact that the available energy for products is 3.6 kcal mol<sup>-1</sup> lower than experiment,<sup>2</sup> as stated above. The width of the distributions obtained from the present calculations does increase with increasing total energy, but not as rapidly as seen in the experimental data of Huber and coworkers.<sup>3</sup> This underestimation of the distribution width is only slight at low energy, but is obvious at 193 nm.

#### IV. Concluding remarks

Classical trajectory simulations of the photodissociation reaction of *sym*-triazine over a range of photon energies have been presented and compared with the available experimental data. The simulations are based on a number of major assumptions. Firstly, we have assumed that the use of classical mechanics is justified since dissociation occurs at energies well above a known barrier to reaction and relatively heavy atom motions are involved in the reaction. Secondly, we have assumed that dissociation can only occur *via* a transition state which is located at a symmetric saddle point for concerted production of three HCN products. Based on this assumption, all trajectories have been initiated in the vicinity of this saddle point, and only trajectories which lead directly to product formation have been analyzed. Trajectories which take the molecule from the saddle point back towards the equilibrium *sym*-triazine configuration were terminated and not considered, since a reactive trajectory would, by assumption, have to pass back to the saddle point and would be considered as initiating at the saddle point. Thirdly, we have assumed that the initial atomic coordinates and momenta for these trajectories are appropriately sampled using a microcanonical normal mode approach. Finally, the dynamics has been based on an interpolated PES<sup>9</sup> which was previously constructed at the BLYP/6-31G\*\* level of theory.

Within this model, we have obtained a number of results. Firstly, the distribution of translational energies of the HCN products, for photodissociation with 295 nm light, is very similar to that calculated from microcanonical sampling of the initial conditions near the saddle point. This suggests that, at least at this energy, the effect of anharmonicity near the saddle point is not a dominant factor in determining the product

energy distribution. Secondly, the calculated average translational energy and average rotational energy of the HCN products are in very reasonable agreement with the most extensive set of experiments. Thirdly, the calculated widths of the HCN translational energy distributions are somewhat smaller than those observed experimentally, although the variation of these widths with energy is qualitatively correct.

The underestimate of the width of the translational energy distributions at higher energy could be due to a (partial) breakdown in the underlying assumptions of the model. The PES was not constructed to describe dynamics far above that for 266 nm light, so some deficiency in the PES for the higher energies must be expected. The harmonic approximation invoked in constructing the initial conditions for the trajectories must also be more restrictive, and hence less reliable, at higher energy. However, the trends of the calculated energy distributions with energy are qualitatively consistent with the observations. Hence, the concerted dissociation mechanism appears to be consistent with the observations. However, at higher energies, the higher activation barrier for the two-step mechanism<sup>7</sup> might be less important,<sup>19,20</sup> so that a contribution of the step-wise mechanism, in which the triazine dissociates through  $C_3N_3H_3 \rightarrow HCN + (HCN)_2 \rightarrow 3HCN$ ,<sup>3,6,7</sup> might broaden the translational energy distribution.

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