

# Collisional Energy Transfer of Highly Excited Polyatomic Molecules. A Statistical Point of View

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Dados sobre transferência de energia por colisão de tolueno altamente excitado, são interpretados em termos estatísticos pela formação de um complexo. Apresenta-se também correlações de  $\langle \Delta E \rangle_{\text{all}}$  com o número total de graus de liberdade interna e a densidade total dos estados vibracionais.

Collisional energy transfer data of highly excited toluene are interpreted in terms of the formation of a statistical collision complex. Correlations of  $\langle \Delta E \rangle_{\text{all}}$  with the total number of internal degrees of freedom and the total density of vibrational states are presented.

**Key words:** *energy transfer; molecules; collisions.*

Energy transfer between highly excited polyatomic molecules in the gas phase is a subject of current interest in chemical kinetics and has been reviewed several times<sup>1-4</sup>. In principle the outcome of a particular collision can be calculated by classical or quantum mechanics. Nevertheless, even for simple systems many difficulties arise and a large amount of computer time is required. Because of that, many simple models have been developed.

As reviewed by Oref and Tardy<sup>4</sup>, many quantitative versions of the statistical model have been presented<sup>5-9</sup>. The fundamental idea is the formation of a "sticky" collisional complex, long lived enough to distribute statistically the total energy. In general, in all these models the transitional modes are sinks for the transferred energy and the quantity  $\langle \Delta E \rangle_{\text{all}}$  depends on the density of states for both colliders, the strength of attractive forces and the total energy of excitation.

The present Note shows how experimental results for a typically highly excited polyatomic colliding with efficient desactivators can be interpreted using these statistical models. The data obtained by Hippler, Troe *et al.*<sup>10</sup> for toluene with an excitation energy of 52000 cm<sup>-1</sup> and colliding with large polyatomic molecules were analysed.

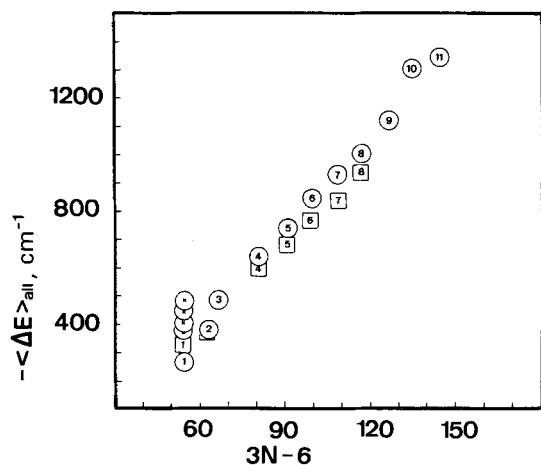
For an ensemble of molecules which behave as strong colliders at equilibrium, a Boltzmann distribution is maintained on each collision. The probability of transferring a

given  $\langle \Delta E \rangle$ , for all initial states  $i, j$  of the colliding molecules is:

$$P(\Delta E) = \frac{\int_0^{\infty} B(E_i) B(E_i + \Delta E) dE_i \int_0^{\infty} B'(E'_j) B'(E'_j - \Delta E) dE'_j}{\int_{-\infty}^{\infty} P(\Delta E) d\Delta E}$$

Here  $B(E)$  is the Boltzmann distribution which can be expressed in terms of  $N(E)$ , the density of vibrational-rotational states. In a previous work, Oref *et al.*<sup>11</sup> obtained an analytical expression for classical densities of vibrational states of large polyatomic molecules. They proposed that the averaged energy transferred per collision is proportional to  $s_r^{1/2}$ , the squared rate of the "reduced" number of vibrational degrees of freedom.

To see if this kind of description applies to excited toluene, we examined if there is any correlation between  $\langle \Delta E \rangle_{\text{all}}$ , the average energy transferred by collision, and the total number of internal degrees of freedom of the collisional complex (Figure 1). The values of  $\langle \Delta E \rangle_{\text{all}}$  were taken from the literature<sup>10</sup> and  $N$  is the total number of atoms of the collisional pair,  $C$ . The number of atoms of toluene is 15, then, if the bath gas is composed of  $m$  atoms,  $N = 15 + m$ . The total number of



**Figure 1.**  $\langle \Delta E \rangle_{all}$  for toluene at 300 K and  $52000 \text{ cm}^{-1}$  as a function of the total number of d.o.f. of the collision complex:  $\circ$  for the  $C_nH_{2n+2}$  series (the number indicates de number of carbon atoms),  $\square$  for the  $C_nF_{2n+2}$  series,  $\circ$  for halogen substituted methane.

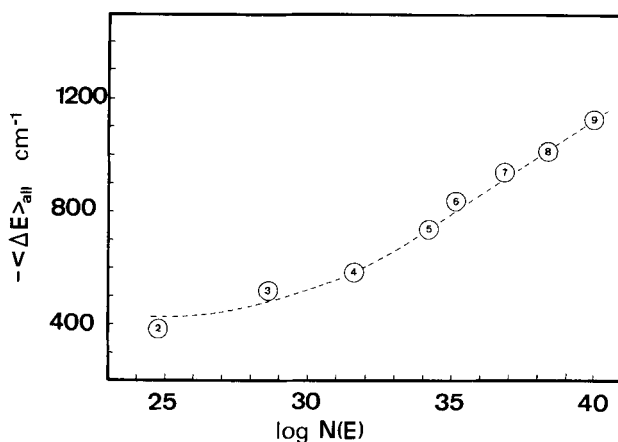
degrees of freedom (d.o.f.) is three times the number of atoms of C, and for a non-linear species the total number of internal (vibrational) d.o.f. is  $v^+ = 3N - 6$ . In fact, the number of internal d.o.f. of C is larger (by 6) than the number of internal d.o.f. of separated toluene + M. That is, there are 3 translational modes and 3 rotational modes that "disappear" when C is formed with a nonlinear polyatomic molecule. They become internal d.o.f. After the collision the molecules toluene and M recover their identity but containing an amount of energy that is different from what it was before the collision. There remains the question if the vibrational energy of toluene is transferred to relative translation, to the rotational modes or to vibrations of M. In this sense, we are presently working in a model in order to solve this point.

In Figure 2 we show the  $\langle \Delta E \rangle_{all}$  values as a function of the total density of vibrational states of C. This quantity is approximated since only the vibrational modes of toluene and M were considered, that is a "super-molecule" having only the vibrational frequencies of isolated toluene and M, and an internal energy of  $52000 \text{ cm}^{-1}$ , was "constructed". At this point no attempt was made to consider the 6 transient vibrational modes of the complex. As it was suggested by one of the reviewers, these 6 d.o.f. are the van der Waals modes of the complex, all of low frequency. Their exclusion from the state density in Figure 2 is in a sense arbitrary, but mandated by the formulae used for the calculation. The addition of these modes will increase the calculated density. Nevertheless, a good correlation is obtained. An equally good correlation would be obtained, one suspects, if these modes were included.

Correlations of collisional data with parameters related to the increasing size of collision partner are in the literature. In general they often have little theoretical basis. The present correlation is related to the properties of the complex. We

interpreted our results as an evidence of the formation of a long lived collision complex where the energy of excited toluene is statistically redistributed within the internal modes. Molecules of three or four atoms do not follow the general trend. Perhaps due to the fact that they are rather "small" molecules and they cannot accommodate large quantities of energy, after the complex breakdown, because of the small number of modes. If the isolated molecules are considered, it can be shown that at a given energy, their densities of states are several orders of magnitude smaller than the density of states of toluene which is not the case of collisional partners shown in Figure 2. Finally, the fact that hydrogenated and fluorinated molecules do not follow a unique correlation is not surprising since the nature of reactant/bath interactions is not a fully resolved question. Certainly, the attractive and repulsive terms in the interactive potentials are different in both cases.

These data form a predictive basis for other collision partners. Other systems are presently being studied and the results will be published in a comprehensive way. Also, we expect that the results of the modelling will provide a better interpretation of these correlations.



**Figure 2.**  $\langle \Delta E \rangle_{all}$  for toluene at 300 K and  $52000 \text{ cm}^{-1}$  as a function of the density (per  $\text{cm}^{-1}$ ) of vibrational states of the collision complex for the  $C_nH_{2n+2}$  series.

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