

LETTERS TO THE EDITOR

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COMMUNICATIONS

Comment on nonstatistical behavior in laser chemistry and chemical activation*

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(Received 6 December 1976)

The recent megawatt ir laser chemistry experiments have raised many interesting theoretical problems regarding the behavior of highly vibrationally excited molecules. Grunwald and coworkers¹ have reported the following:

(i) Several molecules (CCl_3F , CF_3Cl , CHClF_2) were decomposed at 60 torr pressure by a pulsed CO_2 laser with pulse duration of about 200 nsec and intensity of 1.5 MW/cm^2 .

(ii) The conversion per pulse, C , (which is proportional to the reaction rate) was studied as a function of the mean energy absorbed by the molecules (E_{abs}), and the following empirical relation was found to hold in all cases studied¹: $\log C = A - E^*/E_{\text{abs}}$, where A and E^* are constants.

(iii) RRKM theory was applied to these systems¹ with the assumption that the vibrational energy is randomized among all vibrational modes before the reaction takes place (that is $\tau_{vv} < \tau_R$ where τ_{vv} and τ_R are the vibration-vibration relaxation, and the reaction times, respectively). With this assumption it is possible to calculate the vibrational temperature T_v for a given amount of absorbed energy E_{abs} . In the high energy limit (where E_{abs} is so high that the mean vibrational occupation number is greater than 1), we have $E_{\text{abs}} = s K_B T_v$, where s is the number of vibrational modes. Thus, RRKM theory enables us to interpret observation (ii) in terms of the familiar Arrhenius relation of a rate constant vs temperature. However, the values of E^* predicted by RRKM theory are much higher than those found experimentally. In the case of CF_3Cl the experimental E^* was 86 kcal/mole, whereas an RRKM calculation yielded a value of 296 kcal/mole.

(iv) In order to interpret this discrepancy it was suggested¹ that the reverse assumption regarding τ_{vv} (i. e., $\tau_{vv}, \tau_{vT} \gg \tau_R$) applies where τ_{vT} is the vibration-translation relaxation time. Thus collisions are assumed to equilibrate only the pumped mode (as the cross section for resonant $v-v$ exchange is large) but are not capable of randomizing the energy among all modes. On the basis of this model, it is clear that during the relevant time scale ($t < \tau_R$) the vibrational energy is being stored in the pumped mode, and the distribution of levels with-

in the mode is Boltzmann-like with an effective temperature much higher than $E_{\text{abs}}/s k_B$. Thus observation (ii) is again accounted for with a much higher T_v (or much lower E^*) than expected from RRKM, as was found experimentally.¹

One of the disadvantages of this model is that the resonant nature of vv intramode relaxation does not hold for very high vibrational quantum numbers (owing to anharmonicity), and thus the molecule is unlikely to have a single equilibrated mode under these conditions. In addition, this model predicts a strong dependence of the dissociation mechanism on the mode of excitation, a prediction in contrast with recent experimental results.²

In this Communication we suggest a different assumption regarding the time scales of the various processes involved. The assumption based on experimental evidence^{2,3} is $\tau_{vv} < \tau_R \ll \tau_{vT}$ that is, there is a fast redistribution of energy by collisions among all vibrational modes prior to the reaction. However, owing to the slowness of the $v-T$ processes^{4a} (which is an essential condition for obtaining a nonthermal behavior), the vibrational modes are coupled via a *cold translational bath* (at room temperature). This fact leads to the establishment of a (nonstatistical) steady state between the modes (for times less than τ_{vT}) in which energy is distributed nonuniformly among the modes.³⁻⁶ The condition $\tau_R \ll \tau_{vT}$ ensures that the reaction occurs while this steady state is maintained (otherwise, there occurs just the usual thermal reaction).

In order to demonstrate the nature of this steady state let us consider a system of two harmonic oscillators coupled by a Landau-Teller mechanism via a translational bath. Such a system reaches a steady state (provided $\tau_{vv} < \tau_{vT}$) in which each oscillator may be characterized by a different temperature,³⁻⁶ i. e., $(\omega_A/T_A) - (\omega_B/T_B) = (\omega_A - \omega_B)/T$ where T_i , ω_i are the temperature and frequency of oscillator i and T is the bath (translational) temperature.⁷

For an n oscillator system, if one knows the path in which the oscillators are coupled, it is possible to apply this steady state relation for each possible process and find the steady state distribution. Such a model was recently found by McNair *et al.*³ to be in excellent

agreement with their experimental results on $v-v$ transfer in CH_3F .³

Turning now to the ir photochemistry experiments, we note that because of intramolecular coupling (anharmonicities), the concept of modes becomes inapplicable for very high excitation energies; intramolecular energy scrambling and relaxation should be taken into account, and thus the steady-state relation $(\omega_A/T_A) - (\omega_B/T_B) = (\omega_A - \omega_B)/T$ is not expected to hold. For the sake of the present discussion, however, let us assume that we have diagonalized the exact molecular Hamiltonian so that we have a set of uncoupled exact molecular eigenstates. The laser excites these states according to their dipole strengths, thereby yielding a nonstatistical initial distribution. These states are now coupled by collisions only via the cold translational bath. We then argue that a steady state can be established for times $t < \tau_{vT}$, leading to a non-RRKM behavior of the reaction rates, and the argument does not depend on any harmonic assumption.

The main conclusions from the model presented are as follows:

(1) It is known that deviations from statistical behavior may be expected in systems with fast reaction rate compared to internal relaxation ($\tau_R < \tau_{vv}, \tau_{vT}$). We suggest here that the reverse condition ($\tau_{vT} > \tau_R > \tau_{vv}$) may also result in nonstatistical behavior due to the establishment of a nonequilibrium steady state in the system.

(2) Our model in the high-energy limit qualitatively accounts for observation (ii) with a considerable reduction of E^* (relative to RRKM). That is possible if the energy flow path is such that at steady state the energy E_{abs} is stored in a few modes which have the same temperature $T_v = E_{\text{abs}}/k_B s^*$ and the other modes remain cold. Grunwald has found $s^* = 1$ for CClF_3 but for laser enhancement and according to our model s^* may take any value between 1 and s depending on the molecular frequencies and the flow path. A slow $v-v$ model which assumes that the energy remains in the originally pumped mode was suggested by Grunwald *et al.*¹ to interpret their results. We claim here that the reverse assumption (fast vv) may lead to a similar effect (i. e., an effective vibrational temperature much higher than might be expected from statistical models). An interesting point is that either model allows for concentration of energy in a restricted number of modes. However, in the model proposed here the nature of the steady state (which exists for times $t < \tau_{vT}$) does not depend on the way in which energy was pumped into the vibrations.

As an example of the nonstatistical behavior suggested here (not as a direct comparison with experiment) let us consider the CCl_3F molecule. Suppose that the decomposition occurs via the bending modes (say ν_5). We now adapt the following path for energy transfer: $\nu_1 - 2\nu_2$; $\nu_1 - 3\nu_3$; $\nu_1 - \nu_4 - 2\nu_5$; $\nu_2 - 2\nu_6$. Applying the steady state relation for each process we can solve for the energy

stored in each degree of freedom (for the energy stored in each mode multiply by the degeneracy of the mode). With the assumed value $\hbar\omega_5/k_B T_5 = 0.1$ we then have the following values of energy stored in each degree of freedom at steady state (in cm^{-1}): $E(1) = 260$, $E(2) = 460$, $E(3) = 550$, $E(4) = 1570$, $E(5) = 3800$, and $E(6) = 760$. Thus, 80% of the total energy is stored in ν_4, ν_5 . For comparison, the thermal distribution with the same energy in ν_5 is $E(1) = 3500$, $E(2) = 3750$, $E(3) = 3800$, $E(4) = 3600$, $E(5) = 3800$, and $E(6) = 3870$. Thus the total energy in the molecule needs to be two and a half times as much in the thermal distribution for $E(5)$ to be the same in the thermal and nonthermal case!

(3) The present model predicts that the mechanism and yield of the reaction do not depend on the distribution of energy within the molecule upon laser excitation. This prediction, which is in agreement with recent experimental results,² is in contrast to what would be expected from a slow $v-v$ model in which the energy is stored in the initially pumped mode. We emphasize that the issue of whether energy is randomized within the molecule by intramolecular couplings or remains confined to some region in phase space prior to collisions cannot be resolved by the experiments cited, and is irrelevant for our model (i. e., the reaction is assumed to be slow compared to the collisional time τ_{vv} that establishes the nonstatistical steady state).

(4) The same model may apply to chemical activation experiments³ where a complex is formed by a reaction and undergoes many collisions before decomposition.

We are grateful to Professor E. Grunwald, Dr. R. McNair, and Professor James L. Kinsey for many helpful discussions.

*This work was supported in part by the National Science Foundation and the Energy Research and Development Administration.

¹(a) E. Grunwald and K. J. Olszyna, *Laser Focus*, June (1976). (b) D. E. Dever and E. Grunwald, *J. Am. Chem. Soc.* **98**, 5055 (1976) and references cited therein.

²It was found by Hill and Grunwald and by Olszyna and Knishanow that the yield and products in megawatt laser experiments were insensitive to the excitation wavelength. Moreover, excitation by energy transfer from SiF_4 yielded similar results. We are grateful to Professor Grunwald for providing us with this information prior to publication.

³(a) R. E. McNair, Ph. D. thesis, Massachusetts Institute of Technology, 1976; (b) R. E. McNair, M. R. Feld, S. P. Fulghum, G. W. Flynn, and B. J. Feldman, *Phys. Rev. Lett.* (submitted).

⁴(a) E. Weitz and G. Flynn, *Ann. Rev. Phys. Chem.* **25**, 275 (1974); (b) D. Siebert and G. Flynn, *J. Chem. Phys.* **62**, 1212 (1975).

⁵C. E. Treanor, J. W. Rich, and R. G. Rehm, *J. Chem. Phys.* **48**, 1798 (1968).

⁶W. D. Breshears, *Chem. Phys. Lett.* **20**, 429 (1973).

⁷Upon completion of this Communication we learned of similar work done by Irwin Shamah and George Flynn [*J. Am. Chem. Soc.* (submitted)].

⁸J. D. Rynbrandt and B. S. Rabinovitz, *J. Phys. Chem.* **75**, 2164 (1971).