

A NOTE ON QUASIEQUILIBRIUM VIBRATIONAL DISTRIBUTIONS OF POLYATOMIC MOLECULES

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The quasiequilibrium vibrational distribution characterizing the intermediate relaxation stage established by near-resonant, inter- and intra-mode collisional V-V exchanges in polyatomic molecules is derived through the maximum entropy principle. When a unique set of dominant energy transfer pathways can be identified one obtains familiar relationships between vibrational mode temperatures. When many nearly equivalent sets are possible the analysis suggests a common vibrational temperature. The validity of the assumptions and the applicability of the results for explaining energy localization in polyatomic molecules following laser excitation are considered.

1. Introduction

The interesting findings of the many recent laser induced chemistry experiments have, naturally, stimulated extensive theoretical efforts[‡]. The results of some experiments in which polyatomic molecules such as CH₃F [3], C₄F₈ [4], CCl₃F and CF₃Cl [5] were vibrationally excited using short CO₂ laser pulses suggest that the absorbed energy is partly localized in certain vibrational modes. To account for this behavior it has been proposed [3,4,6] that several dominant V-V exchange processes lead to a special kind of a quasiequilibrium vibrational distribution. It is assumed that the time scale of these processes, τ_{VV} , is such that $\tau_p < \tau_{VV} \ll \tau_{VT}$ where τ_p is the laser pulse duration and τ_{VT} is the V-T, R relaxation time. The form of the intermediate distribution at $t \gtrsim \tau_{VV}$ is governed by the

limited number of collisional pathways which are assumed to dominate the flow of energy between the vibrational modes. If these processes are not completely resonant a small amount of energy corresponding to the resonance gap is exchanged with the translational-rotational degrees of freedom. Assuming that each mode is characterized by a well defined temperature and its level scheme can be approximated by the harmonic oscillator model then detailed balance relations for the dominant pathways yield simple relationships between the mode temperatures [7,8]. Depending on the set of dominant pathways the translational-rotational temperature, T , and the level spacings the temperatures of different modes, even those with similar frequencies, may be quite different, i.e. vibrational energy may be localized.

The related assumptions of well defined vibrational temperatures, harmonic spacings and $\tau_{VV} \ll \tau_{VT}$ set limitations on the applicability of the above model, especially for high lying levels. Yet, the most severe limitation seems to be the requirement for a limited

[‡] For reviews see e.g. ref. [1]. Reviews by R.V. Ambartzumian, N. Bloembergen, C.D. Cantrell, D.M. Larsen and K.L. Kompa may be found in ref. [2].

number of strong coupling V–V processes. Consider a polyatomic molecule with r nearly harmonic modes with frequencies $\omega_1, \dots, \omega_r$ and degeneracies d_1, \dots, d_r . Suppose for example that $s_i \omega_i \approx s_j \omega_j$ where s_i, s_j , are some small integers (e.g. $\omega_1 \approx 2\omega_2$) so that collisions involving inter- or intramolecular transitions $s_i \omega_i \leftrightarrow s_j \omega_j$ may be assumed to constitute one dominant pathway. Application of the detailed balance principle to this process yields

$$s_i \omega_i / T_i - s_j \omega_j / T_j = (s_i \omega_i - s_j \omega_j) / T, \quad (1)$$

where T_i and T_j are the temperatures of modes i and j . This result was first derived in ref. [7] for a mixture of two diatomic gases ($r = 2, s_1 = s_2 = 1$) and then extended for multiquantum processes and polyatomic molecules in ref. [8] (see also ref. [9]). Similar expressions can be easily derived for multimode transitions such as $q_i \omega_i \leftrightarrow q_j \omega_j + q_k \omega_k$. If, say, $s_i \omega_i = s'_j \omega_j$ where $s'_j \neq s_j$ (e.g. $s'_j = s_j + 1$ where $s'_j \omega_j \gtrsim s_i \omega_i \gtrsim s_j \omega_j$) then application of (1) leads to the conclusion that either the assignment of vibrational temperature is not justified or that $T_i = T_j = T$, i.e. complete equilibrium. More generally, if the set of dominant pathways includes more than $r - 1$ independent processes then at least two vibrational temperatures are equal.

This note has two related objectives. First, to derive the quasiequilibrium distribution corresponding to the above model via the maximum entropy principle. This procedure requires specification of constraints on the intermediate equilibrium state and provides a more general framework for incorporating physical assumptions and judging their implications. Our second objective is to consider the assumptions involved in the simple model outlined above and to point out some necessary modifications when these assumptions are not valid.

2. The quasiequilibrium distribution

Any equilibrium or quasiequilibrium distribution of the polyatomic gas can be obtained by maximizing the generalized entropy function [10, 11]

$$S = -k \int d\epsilon \sum_{\mathbf{v}} P(\epsilon, \mathbf{v}) \ln [P(\epsilon, \mathbf{v}) / D\rho(\epsilon)], \quad (2)$$

subject to appropriate constraints. Here k is the Boltzmann constant, $\epsilon = \epsilon_{\text{trans}} + \epsilon_{\text{rot}}$ is the sum of translational and rotational energies of the molecule.

$\mathbf{v} = v_1, \dots, v_r$ specifies the entire vibrational state of the molecule, $P(\epsilon, \mathbf{v}) d\epsilon$ is the joint probability of finding the molecule with translational–rotational energy between ϵ and $\epsilon + d\epsilon$ and with vibrational states v_1, \dots, v_r , $D = \prod d_i$ is the overall vibrational degeneracy and $\rho(\epsilon)$ is the density of translational–rotational states. (In the classical rigid rotor approximation $\rho(\epsilon) \propto \epsilon^\alpha$ with $\alpha = 3/2$ and 2 for linear and nonlinear molecules, respectively.) The maximization procedure amounts to finding the probability distribution function $P(\epsilon, \mathbf{v})$ which maximizes S subject to the normalization

$$\int d\epsilon \sum_{\mathbf{v}} P(\epsilon, \mathbf{v}) = 1 \quad (3)$$

and any additional constraints. The extremal P and S are, respectively, the equilibrium distribution and the equilibrium entropy (per molecule). If the only constraint besides (3) is that the average energy per molecule is constant, i.e.

$$\langle E \rangle = \langle \epsilon \rangle + \sum_{i=1}^r \langle E_{v_i} \rangle = \text{const}, \quad (4)$$

then $P(\epsilon, \mathbf{v}) = D\rho(\epsilon) \exp(-\beta E) / Q(\beta)$ is the equilibrium Boltzmann distribution and $S = k \ln Q - \langle E \rangle / T$ is the entropy per molecule in the canonical ensemble; $\beta = 1/kT$, and Q is the canonical partition function per molecule. Note that in expressing the vibrational energy in (4) as a sum of mode energies it is assumed that anharmonic intermode couplings can be ignored. This assumption which may not hold for highly excited levels will be retained throughout the discussion. Also, for convenience, we assume $\omega_1 \leq \omega_2 \leq \dots \leq \omega_r$.

The derivation of (1) requires an additional constraint besides (3) and (4). The formulation of this constraint involves an r -dimensional vector of integers $\mathbf{n} = n_1, n_2, \dots, n_r$, the specification of which is equivalent to choosing a set of dominant pathways. The correspondence is achieved by the requirement that transitions such as $s_i \omega_i \leftrightarrow s_j \omega_j$ or $q_i \omega_i \leftrightarrow q_j \omega_j + q_k \omega_k$ are considered dominant if and only if $s_i n_i = s_j n_j$, $q_i n_i \leftrightarrow q_j n_j + q_k n_k$ etc. It is not difficult to verify that among the infinity of transitions which fulfill these conditions only $r-1$ are linearly independent. The constraint imposed by the dominant pathways on the distribution is

$$\langle V \rangle \equiv \sum_{i=1}^r n_i \langle v_i \rangle = \text{const}. \quad (5)$$

To visualize this constraint consider for example a collision inducing the intramolecular transition $s_i \omega_i \rightarrow s_j \omega_j$. After the collision $v'_i = v_i - s_i$ and $v'_j = v_j + s_j$ but since $n_i s_i = n_j s_j$ we get $n_i v'_i + n_j v'_j = n_i v_i + n_j v_j$. The quantity V may be considered as the effective number of quanta per molecule. In the case of diatomic molecules (5) reduces to the constraint leading to the Treanor distribution [7, 11].

Before proceeding in the derivation let us consider the significance of (5) and (4). Eq. (5) is physically meaningful if there is only one possible vector n_1, \dots, n_r or equivalently if no more than $r-1$ independent pathways (and their linear combinations) dominate the V-V exchange. One simple way for choosing the n_i^m 's is to rely on the common notion that fast V-V processes can be identified by their small resonance defects (thereby disregarding other factors, such as symmetry, whose influence is usually unknown).

In this case one may introduce some basic, or common divisor, frequency ω and determine the n_i 's by minimizing $|\omega_i - n_i \omega|$. The dominant pathways then obtain as linear combinations of the r basic transitions $\omega_i \rightarrow n_i \omega$. (Note that for $\omega < \omega_i$ these "virtual" transitions describe $r-1$ independent real transitions. Similarly, if $\omega = \omega_i$, i.e. $n_i = 1$, we also have $r-1$ real transitions.) As a specific example which also illustrates the difficulties consider the CCl_3F molecule whose fundamental frequencies are [12], $\omega_1, \omega_2, \dots, \omega_6 = 241, 350, 394, 535, 847, 1085 \text{ cm}^{-1}$; ω_1, ω_3 and ω_5 are doubly degenerate. Choosing, say, $\omega = 115 \text{ cm}^{-1}$ we find $n_1, \dots, n_6 = 2, 3, 3, 5, 7, 9$. This choice allows for example $\omega_2 \leftrightarrow \omega_3$ ($|\Delta E| = 44 \text{ cm}^{-1}$), $\omega_4 \leftrightarrow \omega_1 + \omega_2$ (56), $\omega_6 \leftrightarrow \omega_1 + \omega_5$ (3) or $\omega_5 \leftrightarrow \omega_1 + \omega_4$ (71), but excludes other near resonant transitions such as $\omega_6 \leftrightarrow 2\omega_4$ (15) or $\omega_4 \leftrightarrow 2\omega_1$ (53). Moreover, this scheme includes many less resonant transitions, e.g. $\omega_4 \leftrightarrow \omega_1 + \omega_3$ (100). The ambiguities become obvious if one notes that slightly different but not less reasonable choices such as $n_1, \dots, n_6 = 2, 3, 3, 4, 7, 9$ ($\omega = 125 \text{ cm}^{-1}$) or $2, 3, 3, 5, 8, 10$ ($\omega = 110$) would allow and exclude different near resonant transitions. (The choice demonstrated in ref. [6] is equivalent to $n_1, \dots, n_6 = 1, 1, 2, 2, 3, 4$ with $\omega_i = n_i \omega_1$. It does not correspond to $|\omega_i - n_i \omega_1| \rightarrow \min$ and reflects again the variety of possible schemes.) In several cases the identification of a dominant n is unambiguous, see below.

The constants in (4) and (5) are determined by the

initial conditions, which for short pulse laser excitation experiments refer to $t \geq \tau_p$. If for instance at $t = 0$ the system was in equilibrium at T_0 and the laser pulse selectively excites the k th mode then, using obvious notation, $\langle E \rangle = \langle E \rangle_0 + \langle E \rangle_{\text{abs}}$ and $\langle V \rangle = \sum n_i \langle v_i \rangle_0 + n_k \langle v_k \rangle_{\text{abs}}$. For nonlinear molecules with small rotational spacings $\langle E \rangle_0 = 3kT_0 + \sum \langle E_{v_i} \rangle_0$, $\langle E_{v_i} \rangle$ and $\langle V \rangle$ can be estimated by the harmonic oscillator model, e.g. $\langle E_{v_i} \rangle \approx \hbar \omega_i \langle v_i \rangle \approx 0$ when $kT_0 / \hbar \omega_i \ll 1$. Note that in using (4) as a constraint it is assumed that the polyatomic molecules do not exchange energy with other species which may be present in the system or with the walls. The inclusion of these possibilities is straightforward. In particular, when the translational-rotational modes are strongly coupled to a heat bath due for example to a buffer gas the constraint (4) should be replaced by $\langle \epsilon \rangle = \text{const.}$, i.e. $T = T_0$.

The probability distribution function which maximizes S subject to the conservation constraints (3), (4) and (5) can be obtained for example in the Lagrange multipliers method. The result is

$$P(\epsilon, \mathbf{v}) = D\rho(\epsilon) \exp(-\beta E - \gamma V) / Q(\beta, \gamma). \quad (6)$$

Using the definition of E and V in (4) and (5) we find

$$P(\epsilon, \mathbf{v}) = P(\epsilon) \prod_{i=1}^r P(v_i) = [\rho(\epsilon) e^{-\beta \epsilon} / q(\beta)] \times \prod_{i=1}^r d_i \exp(-\beta E_{v_i} - \gamma n_i v_i) / q_i(\beta, \gamma). \quad (7)$$

Here β and γ are the Lagrange multipliers conjugated to $\langle E \rangle$ and $\langle V \rangle$, $T = 1/k\beta$ is the translational-rotational temperature in the quasi-equilibrium state. $q(\beta)$, $q_i(\beta, \gamma)$ and $Q(\beta, \gamma) = q(\beta) \prod q_i(\beta, \gamma)$ are the translational-rotational, the i th vibrational and the total partition functions, respectively. Integration of $P(\epsilon, \mathbf{v})$ over ϵ yields the vibrational distribution function $P(v_1, \dots, v_r) = \prod P(v_i)$. For an anharmonic level scheme $E_{v_i} = \hbar \omega_i v_i - x_i \hbar \omega_i v_i (v_i + d_i)$ each $P(v_i)$ is a Treanor-like distribution [7]. In the harmonic oscillator approximation, $E_{v_i} = \hbar \omega_i v_i$, the individual vibrational distributions have a Boltzmann form

$$P(v_i) = d_i \exp(-\beta_i E_{v_i}) / q_i(\beta_i), \quad (8)$$

with vibrational temperatures $T_i = 1/k\beta_i$ given as

$$\beta_i = \beta + \gamma n_i / \hbar \omega_i. \quad (9)$$

Eq. (1) which represents the transition $s_i \omega_i \leftrightarrow s_j \omega_j$ obtains from (9) and the condition $n_i s_i = n_j s_j$.

The parameters β and γ can be evaluated from

$$\langle E \rangle = -\partial \ln Q / \partial \beta = -\partial \ln q / \partial \beta - \sum_{i=1}^r \partial \ln q_i / \partial \beta$$

$$\approx 3kT + \sum_{i=1}^r \hbar \omega_i / [\exp(\hbar \omega_i / kT_i) - 1], \quad (10)$$

$$\langle V \rangle = -\partial \ln Q / \partial \gamma = -\sum_{i=1}^r \partial \ln q_i / \partial \gamma$$

$$\approx \sum_{i=1}^r n_i / [\exp(\hbar \omega_i / kT_i) - 1], \quad (11)$$

where the last equalities refer to the harmonic oscillator approximation.

Assuming that all the requirements and approximations involved in the derivation of (9), or (1), are valid let us briefly list some simple consequences of this result.

- (i) The vibrational temperatures T_i are all either larger or smaller than T . The vibrations are energy rich, i.e. $T_i > T$ when $\gamma < 0$.
- (ii) For $\gamma < 0$, $T_i > T_j$ if $\omega_i/n_i < \omega_j/n_j$, i.e. if $s_i \omega_i \rightarrow s_j \omega_j$ is endoergic. $T_i = T_j$ only in the case of "exact resonance" $\omega_i/n_i = \omega_j/n_j$.
- (iii) Modes with similar frequencies, $\omega_i \approx \omega_j$, may have very different temperatures and different average energies if $n_i \neq n_j$. (For example using $n_2 = 1$ and $n_3 = 2$ for $\omega_2 = 350$ and $\omega_3 = 394 \text{ cm}^{-1}$ of CCl_3F leads to $\langle E_{v_2} \rangle = 550 \text{ cm}^{-1}$ and $\langle E_{v_3} \rangle = 3800 \text{ cm}^{-1}$, see ref. [6].)
- (iv) If ω_i and ω_j are very different but $\omega_i/n_i \approx \omega_j/n_j$ then modes i and j have similar temperatures but quite different energies (except when $T_i \approx T_j$ is either very high or very low).

3. Discussion and summary

The assumptions involved in the derivation of (9) were (a) $\tau_{VV} \ll \tau_{VT}$, (b) harmonic level spacings, (c) a well defined set of dominant V-V transfer pathways. Note that in the derivation of (9) through the maximum entropy principle the existence of vibrational temperatures is ensured by assumptions (a) and (b) and the fact that intramode V-V processes are consistent with (5).

The three, formally independent, assumptions are closely related on physical grounds which set limits on the applicability of (9) or (1) to real systems. First, because of the growing effects of anharmonicities at highly excited levels the level spacings become narrower, the inter- and intramode V-V defects become larger and consequently the validity of assumptions (a) and (b) for energy rich molecules is very much in doubt. Moreover, if indeed $\tau_{VV} \ll \tau_{VT}$ but the anharmonicities are not negligible, as commonly accepted for the intermediate levels of diatomic molecules (where the so-called "V-V up pumping" mechanism is mainly effective) the vibrational distributions are non-Boltzmann and (7) is more appropriate than (8) and (9). Yet, the most crucial assumption in the derivation is (c). We have seen (for CCl_3F) that there are many equally reasonable distinct assignments of dominant pathways and consequently extremely different sets of T_i 's. This trend is especially pronounced for large and energy rich molecules where the number of near resonant combinations is much larger than r . Thus, if there are many more than $r-1$ independent V-V transfer processes which strongly couple (directly or indirectly) all the r modes we are left with two possibilities. (i) $T_i = T_j \neq T$, (ii) T_i 's do not exist except at $t \rightarrow \infty$ when $T_i = T_j = T$. The latter implies that $\tau_{VV} \approx \tau_{VT}$ so that no quasiequilibrium distribution is established during the relaxation process. Since both theory and experiment indicate that except for highly excited levels $\tau_{VV} \ll \tau_{VT}$ the first possibility seems more likely when all modes are strongly coupled. This means that on the average the loss of vibrational energy through exoergic transitions is balanced by the endoergic ones and the net result is conservation of $\langle E_{\text{vib}} \rangle$. Indeed, replacing (5) by $\langle E_{\text{vib}} \rangle = \text{const.}$ would yield a common T_{vib} for all modes, in accordance with the general thermodynamic rule that strongly interacting systems have equal temperatures. This result implies that instead of using an arbitrary set of n_i 's one should employ $\bar{n}_i \propto \omega_i$. The \bar{n}_i 's remain integral numbers if $\omega = \omega_i/\bar{n}_i$ is sufficiently small. As $\omega \rightarrow 0$ then, in (5), $\langle E_{\text{vib}} \rangle \rightarrow \hbar \omega \langle V \rangle = \text{const.}$ Finally it should be noticed that even when all the vibrational modes have the same temperature some degree of localization may exist as long as this temperature is not larger than each of the vibrational quanta.

In certain cases the identification of a unique set of dominant transitions is possible and the quasiequilibrium distribution corresponding to (1) or (9) may be adequate.

In general this requires that the molecule is not too large and not highly excited so that the number of possible single and multiquantum ("overtone" and "combination") transitions is limited. Especially favourable conditions for the application of (9) occur when the mode frequencies are widely spaced or when the modes can be classified into groups such that each group contains modes with similar frequencies (hence similar temperatures). In the latter case there are two possibilities. First, it is possible to identify a small number of collisional transitions which couple modes of different groups so that (1) or (9) can be used to determine the group temperatures. Essentially, this procedure has been applied [3] in interpreting the results of laser excitation experiments of CH_3F molecules. For this molecule the modes can be grouped ($\omega_1 \approx \omega_4$, $\omega_2 \approx \omega_5$, $\omega_3 \approx \omega_6$) and an almost unique set of intermode transitions has been identified [3]. (Using the conventional notation of CH_3F modes the assignment in our terminology is $n_3 = n_6 = n_2 = n_5 = 1$ and $n_1 = n_4 = 2$; the largest mismatches are $\omega_2 - \omega_6 = 280 \text{ cm}^{-1}$ and $\omega_2 - \omega_3 = 427 \text{ cm}^{-1}$ where $\omega_2 = 1475 \text{ cm}^{-1}$.) The excited mode was ω_3 . Whether ω_3 and ω_1 , ω_4 are indeed strongly coupled via $\omega_3 \rightarrow \omega_6 \rightarrow \omega_2$, ω_5 and then $2(\omega_2, \omega_5) \rightarrow \omega_1, \omega_4$ can only be verified by exciting ω_1 or ω_4 and testing if the same quasi-equilibrium is established.

The second possibility is that some of the groups are only weakly coupled and may be considered as independent. This has been called "intrinsically non-RRKM behaviour" [13]. In this case the energy cannot flow between modes belonging to disjointed groups. Non-RRKM behaviour was suggested as a possible explanation of the apparent (highly specific) energy localization observed in the CCl_3F , CClF_3 experiments of Grunwald et al. [5]. Strong V-V coupling and very different temperatures as implied by (1) were suggested as an alternative explanation [6]. While strong coupling between at least some of the modes seems very reasonable, in view of the above discussion the assignment of very different mode temperatures is highly questionable. It must remain open whether apparent localization is due to another mechanism or a

combination of several mechanisms, since none of the existing explanations is completely satisfactory.

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