

ON THE PROBLEM OF THE DETERMINISTIC CONNECTION BETWEEN THE DISTRIBUTION OF MOLECULES OVER QUANTUM STATES AND VELOCITIES

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Received October 23, 1992*

Considering the process of CO self-broadening as an example it is shown that the strong binary collisions of molecules determine the most probable molecular velocity v_j associated with every quantum number J via the molecular distribution over the quantum states.

In the refined ATCF model described in Ref. 1 we assumed that every internal state of a molecule was characterized by a certain most probable velocity v_j . In this paper, using the CO self-broadening as a concrete example, we confirm the correctness of our assumption that the molecular distribution over velocities is closely connected with the distribution over quantum numbers J .

Let us consider the ideal gas medium. The thermodynamic equilibrium is always established in such a medium due to strong collisions between molecules. Moreover, in accordance with quantum mechanics, the Boltzmann distribution of molecules over quantum states J is reached.^{2,3} At the same time analogous distribution of molecular velocities has never been mentioned in the literature (only the distribution function has been determined).

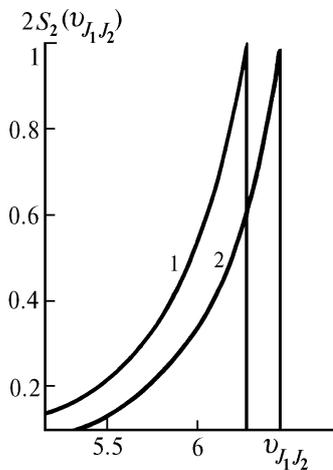


FIG. 1. Probability of strong collisions as a function of the relative velocity for CO colliding molecules with $J_1 = 10$. Two cases were considered: $J_2 = 1$ (1) and 7(2).

Studying the question on the molecular density matrix ρ_j as a function of the most probable velocities v_j , we make use of the fact that strong collisions can change the internal energy of the interacting particles. At the first step we have to show that the most probable relative velocity

$$v_{J_1 J_2} = \sqrt{v_{J_1}^2 + v_{J_2}^2}, \quad (1)$$

depending on the most probable velocities v_{J_1} and v_{J_2} of the two colliding molecules, corresponds to every pair of particles in the states J_1 and J_2 . The highest probability of such collisions is determined by the value $S_2(b_{J_1 J_2}, v_{J_1 J_2}) = 0.5$. With a decrease of $v_{J_1 J_2}$ ($v_{J_1 J_2}^m$) down to zero the probability of such a collision $S_2(v_{J_1 J_2}^m, b_{J_1 J_2}^m)$ lessens down to zero too (see Fig. 1, the case of CO self-broadening for different numbers J). Here we take into account the fact that identical collisions at the same moment of the closest approach of molecules ($t = 0$, see Refs. 4 and 5) occur under the action of an invariable force (in accordance with the principle of conservation of momentum $b_{J_1 J_2} v_{J_1 J_2} = b_{J_1 J_2}^m v_{J_1 J_2}^m = \text{const}$).

Since for a strong collision the condition $S_2 > 0.5$ is not satisfied,^{4,5} $v_{J_1 J_2}^m$ cannot exceed $v_{J_1 J_2}$ and therefore this value is the most probable for the pair of interacting molecules. If we consider now strong collisions of all molecules in thermostat with one molecule being in the state J_1 , then the probability of such collisions is characterized by the sum

$$\sum_{J_2} \rho_{J_2} S_2(v_{J_1 J_2}),$$

where ρ_{J_2} is the fraction of all molecules in the state J_2 in thermostat. When the molecules in the states J_1 collide with thermostat, the probability of strong collisions is determined by the function

$$\bar{S}_2(v_{J_2}) = \rho_{J_1} \sum_{J_2} \rho_{J_2} S_2(v_{J_1 J_2}), \quad (2)$$

depending solely on the velocity of the first molecule. In accordance with the dependences shown in Fig. 1, the value \bar{S}_2 is equal to zero for all $S_2(v_{J_1 J_2}^m = 0) = 0$, that is,

$$\bar{S}_2(v_{J_1}^m = 0) = 0, \quad (3)$$

and for $S_2(v_{J_1 J_2}^m = v_{J_1 J_2}) = 0.5$ we obtain the relation

$$2\bar{S}_2(v_{J_1}^m = v_{J_1}) = \rho_{J_1}. \quad (4)$$

It follows from Eqs. (3) and (4) that the relative number (ρ_{J_1}) of molecules being in the given quantum state J_1 has the most probable velocity v_{J_1} .

Let us define the dependence $\rho_J(v_J)$ using the CO self-broadening as an example. To this end we take the conditions from the refined ATCF model of collisions

$$\begin{cases} S_2(v_{J_1J_2}, b_{J_1J_2}) = 0.5, \\ v_{J_1J_2} b_{J_1J_2} = \text{const.} \end{cases} \quad (5)$$

Let us consider the case in which the first molecule is in the most populated state $J_{1\text{max}} (J_{1\text{max}} = 7$ for CO at $T = 300$ K), and analyze the change of the average velocity v depending on the values of the most probable velocities of the first and second particles (in accordance with Eq. (4), these are the velocities $v_{J_{1\text{max}}}$ and $v_{J_{2\text{max}}}$) and via the electro-optical parameter q_{CO} – on the interaction potential. In the case of the self-broadening there is no difference which of the velocities $\bar{v}_1 = \sum_{J_1} \rho_{J_1} v_{J_1}$ or $\bar{v}_2 = \sum_{J_2} \rho_{J_2} v_{J_2}$ is taken; therefore, we take \bar{v}_2 , which depends on the set of the relative velocities $\{v_{7J_2}\}$ and the velocity of the first

particle v_7 (see Ref. 6), when the first molecule is in the state $J_1 = J_{1\text{max}} = 7$, in accordance with the formula

$$\bar{v}_2 = \sqrt{\left(\sum_{J_2} \rho_{J_2} v_{J_1J_2}\right)^2 - v_{J_1}^2}. \quad (6)$$

It is quite clear from columns 1, 3, and 7 of Table I that the average velocity \bar{v}_2 is practically independent of the most probable one v_{J_1} . When the most probable velocity of a molecule in thermostat $v_{J_{2\text{max}}} = 4.22 \cdot 10^4$ cm/s and when $v_{J_{1\text{max}}}$ is changed significantly (approximately by 30%), the average velocity \bar{v}_2 varies very weakly (approximately by 2%). However, the obtained values in columns 5 and 9 of Table I show that the value \bar{v}_2 depends strongly on the most probable velocity $v_{J_{2\text{max}}}$. A noticeable change in q affects $\bar{v}_{J_1J_2}$ and \bar{v}_2 insignificantly (variation of \bar{v}_2 is within the calculational error, see Table I, columns 3, 5 and 8, 9). This indicates the absence of the obvious dependence of the average velocity \bar{v} on the electrostatic parameters, as in the experiment [see Eq. (6)]

$$\bar{v}_{\text{exp}} = \sqrt{8kT/\pi m}. \quad (7)$$

TABLE I. The values of $\bar{v}_2 \times 10^4$ cm/s of CO molecules as functions of the parameters of velocities and quadrupole momentum (q_{CO} , D Å) for the state of an absorbing molecule $J_{1\text{max}} = 7$ ($T = 300$ K).

$v_{J_{1\text{max}}}$	$q_{\text{CO}} = 8.0$				$q_{\text{CO}} = 5.0$			
	$v_{J_{2\text{max}}} = 4.22$		$v_{J_{2\text{max}}} = v_{J_{1\text{max}}}$		$v_{J_{2\text{max}}} = 4.22$		$v_{J_{2\text{max}}} = v_{J_{1\text{max}}}$	
	\bar{v}_{7J_2}	\bar{v}_2	\bar{v}_{7J_2}	\bar{v}_2	\bar{v}_{7J_2}	\bar{v}_2	\bar{v}_{7J_2}	\bar{v}_2
3.7	6.15	4.91	5.72	4.36	6.04	4.77	5.66	4.28
4.22	6.52	4.97	6.52	4.97	6.38	4.78	6.38	4.78
4.5	6.73	5.0	6.92	5.26	6.55	4.76	6.75	5.03
4.9	7.01	5.01	7.46	5.62	6.84	4.77	7.25	5.34

Table II. The values of the relative most probable velocities $v_{7J_2} \times 10^4$ cm/s for strong collisions of CO molecules at $T = 300$ K.

J_2	0	1	2	3	4	5	6	7	8	9
v_{7J_2}	6.09	6.21	6.19	6.11	6.31	6.38	6.19	5.97	6.19	6.43
J_2	10	11	12	13	14	15	16	17	18	19
v_{7J_2}	6.48	6.44	6.65	6.93	7.23	7.44	7.59	7.68	7.73	7.73
J_2	20	21	22	23	24	25	26	27	28	29
v_{7J_2}	7.73	7.73	7.76	7.76	7.76	7.76	7.76	7.76	7.76	7.77

Thus the calculated results for the most probable velocities v_J of CO molecules show (see Table I) that the average velocity \bar{v} (in the case of CO molecules in thermostat) depends strongly on the most probable velocity $v_{J_{\text{max}}}$ of the molecules being in the most populated state J_{max} . Moreover, this dependence

$$\bar{v} \cong 2v_{J_{\text{max}}} / \sqrt{\pi} \quad (8)$$

is in complete agreement with the experimental Maxwell one.

Thus, for CO ($T = 300$ K), when $v_{J_{\text{max}}} = 4.22 \cdot 10^4$ cm/s, the numerically estimated average velocity $\bar{v} = 4.97 \cdot 10^4$ cm/s is close to $\bar{v}_{\text{exp}} = 4.76 \cdot 10^4$ cm/s.

Table II presents the values of the relative velocities v_{7J_2} obtained according to our collisional model^{1,6} using the value $v_{J_{2\text{max}}} = 4.22 \cdot 10^4$ cm/s coinciding with the maximum value v_{exp} of all the most probable velocities of CO molecules

$$v_{\text{exp}} = \sqrt{2kT/m}. \quad (9)$$

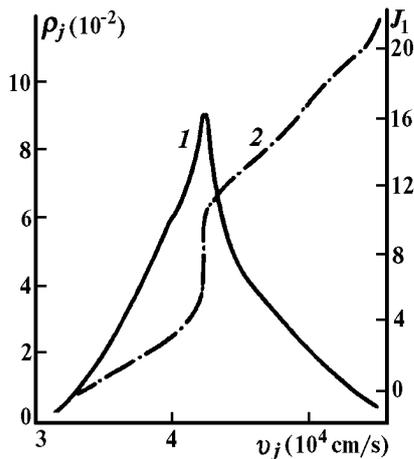


FIG. 2. Velocity distribution of CO molecules at $T = 300$ K: 1) $\rho_j(v_j)$ and 2) v_j .

Therefore, the most probable velocity $v_{j_{\max}}$ of a concrete gas molecule in the most populated state J_{\max} is equal to that the Maxwell distribution. Using this fact we find the molecular distribution over the most probable velocities of CO molecules [see Fig. 2, $\rho_j(v_j)$]. This distribution clearly indicates the

region of the most populated states (for the states with $J = 5-10$ the populations are highest). The most probable velocities close in values to the most probable velocity $v_j = 4.22 \cdot 10^4$ cm/s (the dependence v_j) correspond to these states J .

Thus, strong collisions determine not only the parameters of broadening and shift of a spectral line but also the most probable velocity v_j associated with every quantum state of molecules with the quantum number J via the distribution $\rho_j(v_j)$. In this case the average and most probable velocities obtained numerically using the refined ATCF model for the molecule having a large momentum agree with the analogous characteristics obtained from the Maxwell distribution.

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