CRITICAL ANALYSIS OF MODELS FOR LINE BROADENING IN THE CONTEXT OF FULFILMENT OF THE PRINCIPLE OF CONSERVATION OF MOMENTUM

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Indistinguishable binary strong molecular collisions at the instant of the closest approach ($t = 0$) when contribution of such collisions to the cross section is maximum are illustrated by the example of CO self–broadening. An analysis of indistinguishable collisions shows that only our refined Anderson–Tsao–Curnutte–Frost (RATCF) model adequately describes these collisions and hence the representation of the principle of conservation of momentum for the RATCF model is correct.

In the most popular theories of line broadening proposed by Anderson–Tsao–Curnutte (ATC)[1,2] and Robert–Bonamy (RB)[3] at the stage at which the ATC model was employed the condition of existence of strong binary molecular collisions (SBMC) with the differential cross section S_2 approaching unity was used, i.e.,

$$S_2(b, \upsilon) = 1 , \qquad (1)$$

where b is the shortest distance between molecules and υ is the relative velocity of molecules in collision. The condition of strong collisions [Eq. (1)] implies[1,2] that in these collisions the effects of the interaction potential at time $t = 0$ are equal (there occurs radiation discontinuity or phase distortion[1,2]). Hence, at the instant of the closest approach ($t = 0$) of colliding particles the strong binary interactions occur under the action of the same force. Only in this case the fundamental principle of mechanics, i.e., the principle of conservation of momentum (PCM) is obeyed that can be illustrated by the example of indistinguishable collisions. In this context, it is of interest to examine the fulfilment of the PCM for the models of ATC,[1,2] RB,[3] and RATCF.[4] The paper discusses this very problem.

To do this, let us consider a molecular medium with random molecular collisions. Since the intermolecular potentials of binary interactions in the theory of line broadening[1,2] are represented in the spherical system of coordinates, the field of intermolecular forces is centrally symmetric.[5] The SBMC under the action of the same van–der–Waals central force (SVDWCF) obeys the PCM. In addition, when several forces act on the particles, the SVDWCF can be represented as a resultant of these forces. Then the examined medium is determined solely by the ordered collisions of particles.

Depicted in Fig. 1 is the diagram of action of the SVDWCF from the point O in strong binary collisions of CO molecules. The distances $b_{12} = AO$, $b_{12}^0 = OB$, $b_{12}' = OC$, $b_{12}'' = OD$, and $b_{12}''' = OE$ determine the changes in the coordinates of the centroid of interacting molecules about the point O. The dots on the broken line ABCDE denote the instants of strong collisions at which the closest approach of molecules (at the distances b) occurs for the velocities of relative motion (υ) in the RATCF model[4] and the dots on the broken line A′B′C′D′E′ imply the same but for the ATC model[1,2] for the mean values $\overline{u}$ and $\overline{b}$.

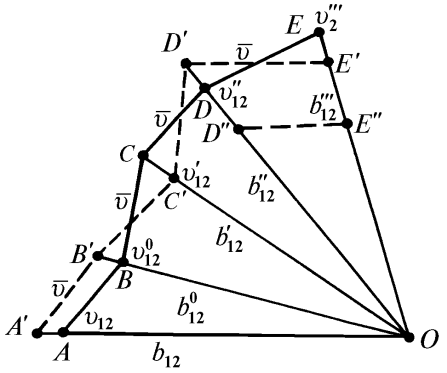

FIG. 1.

In the field of intermolecular forces the collisions of all molecules can be represented in terms of the changes in the coordinates of the centroid of two colliding molecules about the center of action of these forces. As a result of collisions under the action of the SVDWCF not only the arm of the force b, but also the states of interacting molecules change. At least, translational motion of molecules with the most probable relative velocity $\upsilon(J_1, J_2) = \upsilon_{12}$ corresponding to the quantum numbers J_1 and J_2 refers to such states. The PCM for such a system may be written down in the form[1]

$$\upsilon_{12}\, b_{12} = \upsilon_{12}'\, b_{12}' = \ldots = \text{const}. \qquad (2)$$

The application of this principle may be illustrated by the example of indistinguishable collisions for the CO self–broadening. These collisions (Fig. 2) occur with the same force ($\mathbf{F}_{12} = \mathbf{F}_{21}$) for the velocity and distance being unchanged

$$\upsilon_{12} = \upsilon_{21}, \qquad b_{12} = b_{21} \qquad (3)$$

and

$$\upsilon_{12}\, b_{12} = \upsilon_{21}\, b_{21}. \qquad (4)$$

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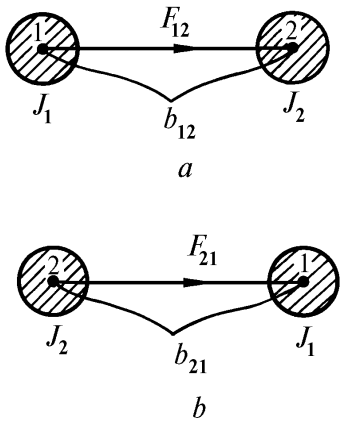

FIG. 2. Types of indistinguishable collisions of molecules: a) M_1 in the J_1 state acts with the force $\mathbf{F}_{21}$ on M_2 in the J_2 state and b) states of molecules are the same as in case (a) but M_2 acts on M_1 with the force $\mathbf{F}_{21}$.

The ATC model which employs conditions (1) and

$$\upsilon_{12} = \overline{\upsilon} \,, \tag{5}$$

where $\overline{\upsilon} = \sqrt{8\,kT/\pi m}$, gives the parameters $\overline{\upsilon}$ and $\overline{b}$ (Table I) for a set of rotational quantum numbers (J_1, J_2). As can be seen from Table I, the ATC model for indistinguishable collisions of CO molecules ($J_1 = 1$, $J_2 = 10$ and $J_1 = 10$, $J_2 = 1$) results in different values of distances ($\overline{b}_0$ ($J_1 = 1$, $J_2 = 10$) = 5.5Å and $\overline{b}$ ($J_1 = 10$, $J_2 = 1$) = 6.48Å) which contradicts the condition of existence of such molecular collisions [Eq. (3)]. Hence, the PCM is violated for the ATC model.

TABLE I. The values of the closest approaches (b,Å) and relative velocities (υ, 10^4 cm/s) in strong collisions of CO–CO *molecules.*

J_1	J_2	Refs. 1, 2			Ref. 4			q_{CO}
			$\overline{b}$	$\overline{\upsilon}$		b	υ	
15	1	*OA*	6.48	6.37	*OA*	6.14	6.36	
15	5	*OB*	5.71	6.37	*OB*	5.36	7.28	
15	7	*OC*	5.5	6.37	*OC*	5.25	7.44	8.0
10	1	*OD*	6.48	6.37	*OD*	6.1	6.36	
1	10	*OE*	5.5	6.37	*OE*	6.1	6.36	
10	1	*OD*	5.08	6.37	–	–	–	
1	10	*OE*	4.3	6.37	–	–	–	5.0

Let us now proceed to an analysis of the same collisions using the RB model. First, the closest approach of two molecules for this model is determined by the relative velocity υ_r and the distance between the molecules r_r (Ref. 3). The principle of conservation stated in Ref. 3 has the form

$$\upsilon_r\, r_r(\text{LJF} + \text{SVDWCF}) = \overline{\upsilon}\,\overline{b}(\text{SVDWCF}) \,. \tag{6}$$

The terms in parentheses of Eq. (6) denote the forces under the action of which colliding molecules with the parameters υ_r, r_r and $\overline{\upsilon}$, $\overline{b}$ move. For the parameters $\overline{\upsilon}$ and $\overline{b}$ to change (for the trajectory to be bend[3]), in addition to the SVDWCF a new Lennard–Jones force (LJF) was introduced into the RB model. As has been already shown in Ref. 6 and in this paper, for a system of particles (in our case of two particles) the PCM is obeyed only in the case in which this system is under the action of the invariable force. Therefore, there are only two possible representations of the conservation principle

$$\upsilon_r\, r_r(\text{SVDWCF}) = \overline{\upsilon}\,\overline{b}(\text{SVDWCF}) \tag{7}$$

or

$$\upsilon_r\, r_r(\text{SVDWCF} + \text{LJF}) = \overline{\upsilon}\,\overline{b}(\text{SVDWCF} + \text{LJF}) \,,$$

neither of the two agrees with Eq. (6). Thus, the PCM in the form of Eq. (6) is incorrect. Second, in the RB model for indistinguishable collisions condition (3) must be satisfied ($\upsilon_{r\,12} = \upsilon_{r\,21}$ and $r_{r\,12} = r_{r\,21}$) from which is follows that

$$\overline{b}(J_1, J_2) = \overline{b}(J_2, J_1) \,. \tag{8}$$

This condition, as has already been noted, is violated for the ATC model (see Table I).

For the same case of the CO–CO collisions our RATCF model[4] provides a set of velocities $\{\upsilon_{12}, \upsilon_{21}, \ldots\}$ (Table II) which are determined in terms of the most probable velocities υ_1 and υ_2 of the first and second particles

$$\upsilon_{12} = \sqrt{\upsilon_1^2 + \upsilon_2^2} \,. \tag{9}$$

In the determination of the velocities υ_{12}, in addition to Eq. (9), we used formulas (1) and (2) and the analytical relation for the most probable velocity $\upsilon_{J\,\max} = \sqrt{2\,kT/m_{CO}}$ (Ref. 5), corresponding to the most populated quantum state of CO molecule. As can be seen from Table II, for different collision types, when the quantum number changes to ten, we obtain a symmetric matrix of the elements $\upsilon(J_1, J_2)$. Such a form of matrix supports the presence of indistinguishable collisions of CO molecules (the equality $\upsilon(J_1, J_2) = \upsilon(J_2, J_1)$ is satisfied for arbitrary values of J_1 and J_2, see Table II). This indicates once again the correctness of the representation of the PCM [Eq. (2)] for our RATCF model and of the diagram shown in Fig. 1 (arrangement of the broken line ABCDE about the point O of application of the SVDWCF).

Table II. The values of $\upsilon_{J_1 J_2}$ for CO *self–broadening in the ground vibrational state* (10^4 cm/s).

J_1	J_2									
	1	2	3	4	5	6	7	8	9	10
1	5.70	5.67	5.77	5.80	5.83	6.04	6.21	6.31	6.34	6.34
2	5.67	5.67	5.80	6.00	6.00	5.99	6.19	6.38	6.51	6.55
3	5.77	5.80	5.77	5.97	6.15	6.15	6.12	6.31	6.53	6.66
4	5.80	6.00	5.97	5.90	6.10	6.31	6.31	6.27	6.47	6.69
5	5.83	6.00	6.15	6.10	5.94	6.15	6.38	6.42	6.34	6.56
6	6.04	5.99	6.15	6.31	6.15	5.97	6.19	6.42	6.47	6.38
7	6.21	6.19	6.11	6.31	6.38	6.19	5.97	6.19	6.45	6.48
8	6.31	6.38	6.31	6.27	6.42	.642	6.19	5.97	6.19	6.45
9	6.34	6.51	6.53	6.47	6.34	6.47	6.45	6.19	5.97	6.19
10	6.34	6.55	6.66	6.69	6.56	6.38	6.49	6.45	6.19	5.97

Thus, the comparison of the ATC, RB, and RATCF models for line broadening from the viewpoint of the PCM fulfilment for indistinguishable collisions of CO molecules shows the following. First, the use of the mean values ($\overline{v}$ for the ATC and RB models) for description of the specific strong molecular collisions leads to the errors in determining the distance of the closest approach of molecules and, consequently, to the violation of the PCM. However, in some cases in which the values of the mean differential cross section $\overline{S}_2^{\mathrm{ATC}}(J_1) = \sum_{J_2} S_2^{\mathrm{ATC}}(\overline{v}, \overline{b}, J_1, J_2)$ are close to the true value of $\overline{S}_2$ the ATC model[1,2] may yield the broadening parameter coinciding with the exact result.

Second, the incorrect representation of the PCM (RB model) also leads to wrong values of the parameters v_r and r_r and hence to errors in determining the cross sections of collisions and the parameters of the broadening.

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