Comment on the Quantum Mechanical Collinear Model of Three Body Rearrangement Scattering

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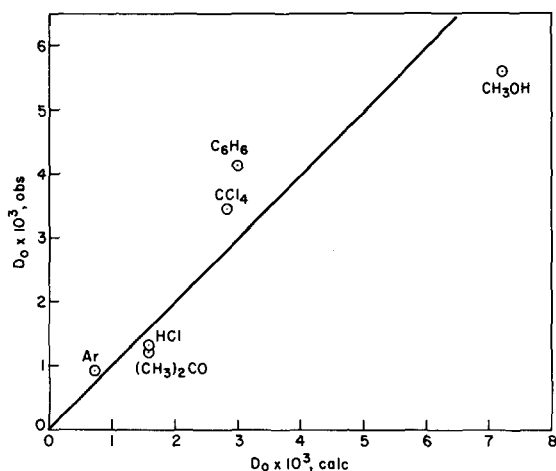
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FIG. 1. Observed vs calculated pre-exponential factors for diffusion (D_0). Calculated values of D_0 are obtained from Eqs. (1) and (3) using the observed barrier height and the calculated values of w.

position and then reverses velocity is neglected in the derivation of Eq. (1). Equation (1) holds for a "hard" collision time equal to the mean time to move from an occupied lattice site to a vacancy. Equation (1) was shown to give good results for simple liquids such as argon and fluorine with $\bar{s}_0 = 0$ but required a finite value of $\bar{s}_0$ for more complex liquids.

It was noted[1] that $\bar{\epsilon} = \bar{\epsilon}_0 - T\bar{s}_0$ would be expected, to first approximation, to depend on temperature as follows:

$$\bar{\epsilon} = \bar{\epsilon}_L(1 - p_v), \qquad (2)$$

where $\bar{\epsilon}_L$ is a mean free energy averaged over the cell volume for a hypothetical liquid without vacancies, and $p_v = \exp(-w/kT)$. By differentiation of Eq. (2) with respect to temperature at constant pressure, it

follows that

$$\bar{s}_0 = \bar{\epsilon}' w p_v' / R T_m{}^2 (1 - p_v'), \qquad (3)$$

where the temperature dependence of $\bar{\epsilon}_L$ has been omitted, T_m is the melting temperature, and the prime on p_v and $\bar{\epsilon}$ signifies that these quantities are to be evaluated at T_m. Earlier the entropy of activation had been evaluated by comparison of values of the pre-exponential factor for self-diffusion (D_0) given by Eq. (1) with the experimental values. It was clear that there was an apparent "compensation effect," i.e., $\bar{s}_0$ increased roughly in proportion to $\bar{\epsilon}_0$. Equation (3) predicts such an effect and, in addition, has a weak (since $w \sim R T_m$) dependence of $\bar{s}_0$ on w.

$\bar{s}_0$ given by Eq. (3) has been evaluated for a number of representative liquids for which gas phase collision diameters[2] are available. The quantity w was evaluated by arithmetic averaging of values of w obtained from liquid density,[1,3] compressibility,[1,3] and the scaled particle theory of liquids.[4] These sources of w usually did not deviate by more than about 20% or so from the arithmetical mean value of w. Calculated values of D_0 are compared with observed values in Fig. 1; the straight line represents perfect correlation between the observed and calculated values of D_0. The agreement between the observed and calculated values of D_0 is reasonably good and demonstrates that the quasi-lattice model of liquids, idealized as it may be, is useful in correlating properties of dense fluids.

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.
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[2] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964).
[3] D. E. O'Reilly and E. M. Peterson, J. Chem. Phys. 55, 2155 (1971).
[4] (a) H. Reiss, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. 31, 369 (1959); (b) H. Reiss, H. L. Frisch, E. Hefland and J. L. Lebowitz ibid. 32, 119 (1960).

Comments

Comment on the Quantum Mechanical Collinear Model of Three Body Rearrangement Scattering*

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We wish to comment on a recent paper by Robinson[1] which dealt with a model for three body reactive scattering. The model system was first considered in a paper by Hulburt and Hirschfelder.[2] The details of the model are given in those papers and need not be repeated here. The results of the Hulburt and Hirschfelder treatment at certain energies were recently questioned as a result of numerical calculations of Tang, Kleinman, and Karplus.[3] Robinson[1] showed that if one examines the Schrödinger equation for the model

system, the basic set used by Hulburt and Hirschfelder[2] is incomplete at these energies. In his study, Robinson applied a limiting procedure to obtain the new basic functions required to obtain the correct algebraic equations determining the transmission and reflection coefficients T_n and R_n. Robinson's[1] results were employed by Dion, Milleur, and Hirschfelder[4] to calculate the transmission and reflection coefficients and their results are in complete agreement with those of Tang, Kleinman, and Karplus.[3]

We would like to suggest that whether or not new basic functions need to be introduced is dependent on the point in the analysis at which the energy is permitted to approach a "resonance" energy.[3] The basic set employed by Hulburt and Hirschfelder[2] can be used to obtain their usual coupled equations involving the transmission and reflection coefficients. Then Robinson's results[1,4] can be obtained from these equations by solving them for the T_n and R_n and then letting the energy approach a resonance value.

As a simple illustration, we consider the problem where one vibrational state in the nonreactive and reactive channels are open. The wavefunction in the three regions of interest may be written as

$$\psi_{\mathrm{I}} = \sin y [\exp(-ikx) + R \exp(ikx)], \qquad (1)$$

$$\psi_{\mathrm{II}} = A \sin(kx) \sin y + B \sin x \sin(ky), \qquad (2)$$

$$\psi_{\mathrm{III}} = T \sin x \exp(iky), \qquad (3)$$

where

$$k = (E^* - 1)^{1/2}, \qquad (4)$$

and E^* is the total center of mass energy (in units of the ground vibrational state). Applying the boundary conditions one finds

$$\exp(-ik\pi) + R \exp(ik\pi) = A \sin(k\pi), \qquad (5)$$

$$T \exp(ik\pi) = B \sin(k\pi), \qquad (6)$$

$$ik[-\exp(-ik\pi) + R \exp(ik\pi)] = Ak \cos(k\pi) - Ba, \qquad (7)$$

$$ikT \exp(ik\pi) = -Aa + Bk \cos(k\pi), \qquad (8)$$

where

$$a = \frac{2}{\pi} \int_0^\pi \sin y \sin(ky) \, dy. \qquad (9)$$

Elimination of A and B leads to

$$(a/k) \exp(ik\pi) T - R = 1 \qquad (10)$$

and

$$-T + (a/k) \exp(ik\pi) R = -(a/k) \exp(-ik\pi). \qquad (11)$$

These equations are easily solved and the limit as k approaches 1 yields

$$T = -2\pi i/(2\pi i - 3) \qquad (12)$$

for the transmission coefficient. This result is seen to be identical to that obtained by Dion, Milleur, and Hirschfelder[4] for this same one channel case using the new basic functions obtained by Robinson.[1]

[1] P. D. Robinson, J. Chem. Phys. **52**, 3175 (1970).
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[3] K. Tang, B. Kleinman, and M. Karplus, J. Chem. Phys. **50**, 1119 (1969).
[4] D. R. Dion, M. B. Milleur, and J. O. Hirschfelder, J. Chem. Phys. **52**, 3179 (1970).

Errata

Erratum: Vibronic Coupling. VI. Vibronic Borrowing in Cyclic Polyenes and Porphyrin

[J. Chem. Phys. **50**, 4137 (1969)]

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In Sec. V. B.2 (Interference Effects), p. 4147, the last sentence of the third paragraph should read: "An analogous analysis shows that *constructive* interference occurs in the $Q_x(0-1)$ emission."