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## Comment on the Calculation of Rate Constants from Transition-State Theory **FREE**

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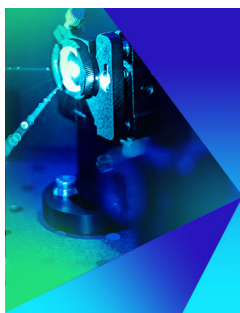


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experimentally whether and how the linewidth depends on the impurity content.

My theory predicts a line shape depending mainly on the shape of the potential well; it is based on a nonlinear coupling and hence the formalism is hard to carry out for the nonlocalized model, but a number of arguments (see my paper) justify this extrapolation.

The question as to which vibrational mode is most likely excited at low temperatures is relevant indeed. The mode which I used in my explanation is only dominant if one can justify (1) the strong-coupling type of theory which I have assumed throughout my paper, and (2) the fact that the vibration, or actually motion, is localized. This is supported by the recognition that the sound velocity, which acts as a measure of the speed with which a distortion would travel, is much smaller than the velocity of light, representing the velocity with which the dipole-dipole interaction travels through the crystal.

### Comment on the Calculation of Rate Constants from Transition-State Theory\*

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AND

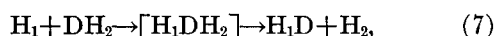
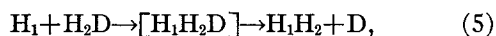
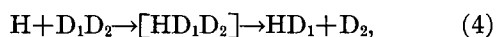
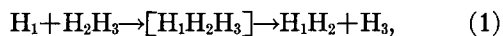
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(Received February 5, 1962)

**I**N the transition state method of calculating reaction rate constants, a statistical factor is introduced by the rotational partition functions of the reactants and the activated complex. The rate constant is of the form  $k = (\mathbf{k}T/h)Q^\ddagger/Q_A Q_B \dots$ , from which this statistical factor is  $\sigma_A \sigma_B \dots / \sigma^\ddagger$ , the ratio of symmetry numbers of the reactants to that of the activated complex.

In the case of exchange reactions between hydrogen atoms and molecules, such as



this statistical factor is simply  $\sigma_m/\sigma^\ddagger$ , where  $m$  indicates the hydrogen molecule. If the transition state is linear and symmetric, as in the recent calculations by Shavitt<sup>1</sup> and Weston,<sup>2</sup> the statistical factors for the above reactions are 2/2, 2/1, 1/1, and 1/2, respectively. This factor remains at the classical limit of high temperature when all quantum effects have vanished, and introduces a classical kinetic isotope effect between reactions

such as (1) and (4). To avoid this untenable conclusion, both Weston and Shavitt introduced a factor of one-half into their rate constants calculated for reactions such as (4) and (7) above. [The reactions affected are (3) to (8) in Shavitt's and Weston's original notation.]

This apparent paradox results from an essential difference between the partition function of the activated complex and that of a normal molecule. In obtaining the partition function of the transition state, one integrates the momentum along the reaction coordinate only from 0 to  $+\infty$ , since negative momenta imply a return of the activated complex to reactants. This means that in the quasi-equilibrium between activated complex and reactants, certain atoms of the complex which appear equivalent (and would be so in a normal molecule) are not. Thus, in reaction (1), the limitation on the direction of motion along the reaction coordinate allows equilibrium between the complex and molecule  $\text{H}_2\text{H}_3$  but not between the complex and  $\text{H}_1\text{H}_2$ . The two equivalent methods of correcting for this are (1) to keep the restriction on the momentum, and admit that the activated complex has lower symmetry, or (2) to keep the "normal" symmetry of the complex, and to integrate the momentum from  $-\infty$  to  $+\infty$ , since the activated complex with equivalent atoms has no memory of which direction it came from. These considerations indicate that the classical statistical factors for the above reactions should be 2/1, 2/1, 1/1, and 1/1. A "collisional" argument, in which one considers the possible ways of bond formation to produce the activated complex and bond breaking to form products from it, leads to an identical conclusion.

The effect these comments have on previous calculations is as follows:

(a) The calculated rate constants  $k_1$  to  $k_8$  in Tables IV, V, and VI of Shavitt's paper<sup>1</sup> should all be doubled. This effect could be offset to some extent by an increase in activation energy, which in Shavitt's calculations was chosen empirically.

(b) The calculated pre-exponential factor given in Section IV of Weston's paper<sup>2</sup> should be doubled, since the rotational contribution is doubled.

(c) The calculated rate constant ratios  $k_2/k_1, \dots, k_8/k_1$  of Shavitt's Table VII and Weston's Table V remain unchanged.

It is apparent that these symmetry arguments do not affect symmetry elements of the transition state which are distinct from the reaction coordinate. Thus, in the exchange reaction  $\text{CH}_4 + \text{H} \rightarrow [\text{H} \dots \text{CH}_3, \dots \text{H}] \rightarrow \text{H} + \text{CH}_4$ , the transition state is probably a planar symmetrical  $\text{CH}_3$  group with the other two hydrogen atoms equidistant from the plane and forming C—H bonds perpendicular to it. The "normal" symmetry number would be six, whereas our arguments imply that it must be reduced to three.

Also, if the equilibrium between activated complex and reactants is as complete as one between normal molecules, the symmetry number need not be changed. This is the case for a reaction such as  $YXY \rightarrow [Y \cdots X \cdots Y] \rightarrow X + 2Y$ , in which the X—Y bonds are symmetrically stretched.

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<sup>1</sup> I. Shavitt, *J. Chem. Phys.* **31**, 1359 (1959).

<sup>2</sup> R. E. Weston, Jr., *J. Chem. Phys.* **31**, 892 (1959).

## Erratum: Ring Closure in a Macromolecule

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[*J. Chem. Phys.* **34**, 1531 (1961)]

ON page 1537 in the expansion for  $C(x)$  for the simple cubic lattice the last term should read  $+41\ 934\ 150x^{11}$ .

## Erratum: Double and Triple Ionization in Molecules Induced by Electron Impact

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[*J. Chem. Phys.* **35**, 575 (1961)]

ON page 579, the formula for the transition probability  $K$  should read

$$K = k! \left\{ \left[ \left( i_2/k \right)^{1/k} - \left( i_1/k \right)^{1/k} \right] / \left( V_2 - V_1 \right) \right\}^k.$$

## Microwave Spectrum and Structure of Trichlorofluoromethane

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(Received December 27, 1961)

THE rotational spectrum of  $CCl_3F$  was measured in the 20 000 to 40 000 Mc/sec range using a Stark modulated spectrograph. Frequency measurements up to 30 000 Mc/sec were accomplished by using standard frequency markers. Above 30 000 Mc/sec use was made of calibrated cavities and the estimated error in this range is  $\pm 3$  Mc/sec. Most of the lines were, however, quite broad and weak, so that even with the frequency markers the weaker lines could only be measured with an accuracy of  $\pm 2$  Mc/sec. The lines of three naturally

TABLE I. Observed and calculated rotational frequencies of  $FCCl_3^{35}$  and  $FCCl_3^{37}$ . Frequencies are calculated with  $B = 2465.76$  Mc/sec and  $B = 2363.4$  Mc/sec, respectively.

Transition $J \rightarrow J+1$	$FCCl_3^{35}$		$FCCl_3^{37}$	
	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)
3→4	18 728±2	19 726.1		
4→5	24 657.6±0.3	24 657.6		
5→6	29 589.3±0.5	29 589.1		
6→7	outside the frequency range of available Klystron		33 087±4	33 087.6
7→8	39 454±3	39 454.2	37 815±4	37 814.4

occurring isotopic species,  $CCl_3^{35}F$ ,  $CCl_3^{37}F$ , and  $CCl_2^{35}Cl^{37}F$  were identified in various transitions. The first two as expected, are symmetric top molecules while the latter shows the characteristic spectrum of a slightly oblate asymmetric top molecule. The transitions  $J = 4 \rightarrow 5$  and  $J = 6 \rightarrow 7$  of this species were fully analyzed. The considerable breadth of the lines, 15 Mc/sec in most cases at the lowest pressure used, is probably due to the unresolved splitting of the lines, due to the nuclear

TABLE II. Observed and calculated frequencies of the  $J = 4 \rightarrow 5$  and  $J = 6 \rightarrow 7$  transitions of  $CCl_3^{35}Cl^{37}F$ . Frequencies are calculated with  $A = 2463.7$  Mc/sec,  $B = 2399.3$  Mc/sec and  $C = 1697.2$  Mc/sec ( $b_0 = -0.04385$ ).

Transition	Observed frequency Mc/sec	Calculated frequency Mc/sec
4 <sub>31</sub> →5 <sub>41</sub>	24 172±2	24 173.1
4 <sub>22</sub> →5 <sub>32</sub>	24 243±2	24 245.0
4 <sub>13</sub> →5 <sub>23</sub>		24 297.2
4 <sub>23</sub> →5 <sub>33</sub>	24 301±4 (unresolved)	24 302.0
4 <sub>04</sub> →5 <sub>14</sub> 4 <sub>14</sub> →5 <sub>24</sub>		24 305.4
4 <sub>32</sub> →5 <sub>42</sub>	24 324±2	24 324.2
4 <sub>40</sub> →5 <sub>50</sub>	24 388±2	24 393.9
4 <sub>41</sub> →5 <sub>51</sub>	24 492±2	24 492.6
6 <sub>51</sub> →7 <sub>61</sub>	33 871±3	33 870.9
6 <sub>42</sub> →7 <sub>52</sub>	33 892±3	33 897.5
6 <sub>24</sub> →7 <sub>34</sub> 6 <sub>34</sub> →7 <sub>44</sub>	34 020±3	34 019.4
6 <sub>15</sub> →7 <sub>25</sub> 6 <sub>25</sub> →7 <sub>35</sub>	34 024±3	34 025.7
6 <sub>06</sub> →7 <sub>16</sub> 6 <sub>16</sub> →7 <sub>26</sub>	34 032±3	34 028.9
6 <sub>52</sub> →7 <sub>62</sub>	34 085±3	34 085.6

(Other lines are outside the frequency range of available Klystron.)