

small. Likewise, the nitrogen hyperfine splittings are uniform with the exception of isopropylamine radical.

One would expect that the three-electron  $\pi$  bond between the nitrogen and the trigonal carbon which is implied by the observed spin density delocalization would tend to stabilize a planar structure. However, the effect of atoms with electronegativity greater than 2.3 (electronegativities: H=2.1, C=2.5, N=3.0) bonded to the carbon would be to favor a pyramidal structure, as discussed recently by Pauling.<sup>5</sup> At this stage of the investigation, it is impossible to make a clear choice between the pyramidal and planar structures. However, the "anomalous" nitrogen hyperfine splitting in isopropylamine and proton splitting in diethylamine together with the large temperature dependence observed for the alpha proton splittings in some of the radicals indicate that either the force constant for deformation is quite small and/or that the radicals are actually nonplanar. Experiments are under way to ob-

tain EPR spectral parameters and their temperature dependence for all the radicals in this series in order to answer the very important question of their geometry.

<sup>1</sup> R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.* **45**, 1845 (1966).

<sup>2</sup> A radical of this type has been postulated in the radiolysis of methylamine at 77°K; G. V. Pukhal'skaya, A. G. Kotov, and S. Ya. Pshchetskii, *Dokl. Akad. Nauk. SSSR* **171**, 1380 (1966).

<sup>3</sup> H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.* **28**, 107 (1958), and papers cited therein.

<sup>4</sup> R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.* **39**, 2147 (1963).

<sup>5</sup> L. Pauling, *J. Chem. Phys.* **51**, 2767 (1969).

### Quantum Mechanics of the H+H<sub>2</sub> Reaction: Exact Scattering Probabilities for Collinear Collisions\*

DONALD G. TRUHLAR† AND ARON KUPPERMANN

Division of Chemistry and Chemical Engineering,‡ California Institute of Technology, Pasadena, California 91109

(Received 16 December 1969)

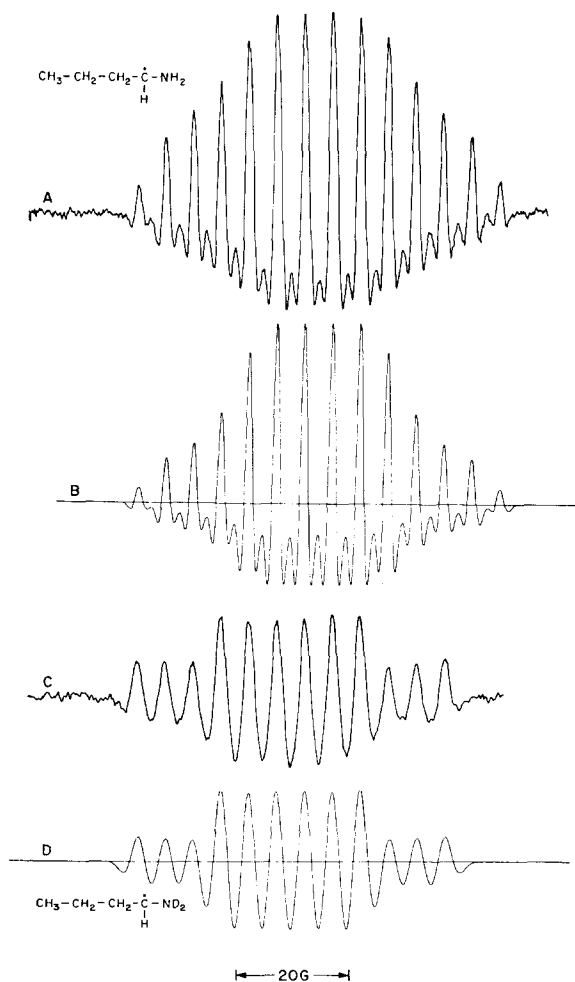


FIG. 1. Second-derivative EPR spectra of radicals from *n*, butylamine (A) and *n*-butylamine-*d*<sub>2</sub> (C) at room temperature—compared with their respective computer simulations (B) and (D).

The H+H<sub>2</sub> reaction is very important in theoretical chemical dynamics.<sup>1-4</sup> A model that is often used to study this reaction is to restrict the atoms to lie on a nonrotating line throughout the collision and to consider that the system is electronically adiabatic, i.e., it remains in its lowest electronic state throughout the whole collision. This reduces the problem to scattering of three particles on a potential energy surface which is a function of two linearly independent coordinates. This model has been studied classically,<sup>5-8</sup> and Mortensen and Pitzer<sup>9</sup> have calculated exact quantum mechanical reaction probabilities at five relative translational energies  $E_0$ . In this Communication, we present some results of our more extensive exact calculations on this model of the H+H<sub>2</sub> reaction and show their consequences for the validity of approximate theories of chemical reactions. For the cases considered here, the assumption of electronic adiabaticity causes very little error.<sup>10</sup>

Other exact quantum mechanical solutions of multi-dimensional models of rearrangement scattering are given in Refs. 9 and 11-15.

The potential energy surface used is the parametrized surface of Wall and Porter.<sup>16</sup> Three parameters are used to fix the Morse curve for H<sub>2</sub> in the asymptotic region, and four parameters are chosen to give the saddle point properties (including barrier height 0.424 eV) suggested by Shavitt<sup>17</sup>; the remaining parameter is adjusted to give a good fit to the position of the minimum energy path for the surface of Shavitt *et al.*<sup>18</sup>

The scattering problem was solved by the finite difference boundary value method (FDBVM) of Diestler and McKoy<sup>14</sup> with a few modifications.<sup>19</sup> We analyzed the numerical solutions  $\chi_i$  in terms of approximate reactance matrix elements,<sup>20</sup> symmetrized

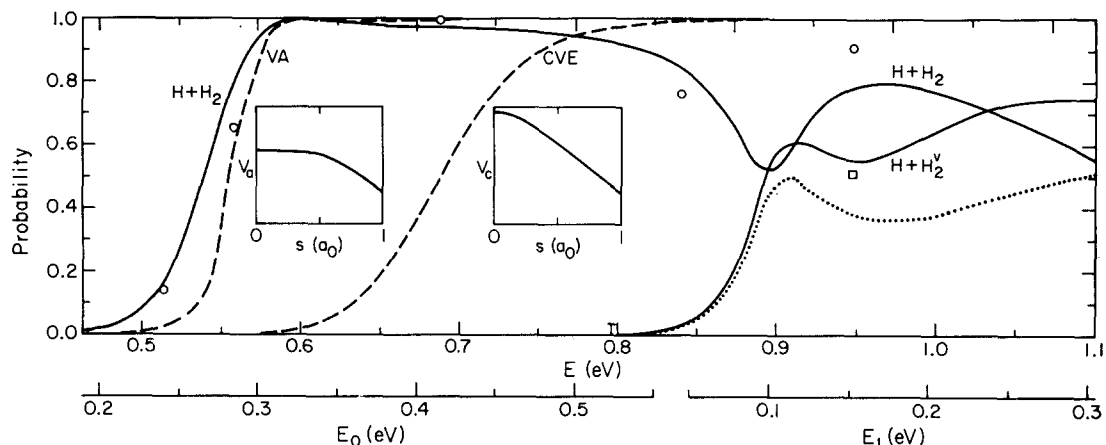


FIG. 1. Probability of reaction (solid lines are from numerical calculation in two mathematical dimensions and dashed lines are from calculations in one mathematical dimension) and probability of nonadiabatic transitions (dotted line) vs total energy ( $E$ ) and relative translational energy ( $E_0$  and  $E_1$  for reactants which are the vibrationally unexcited  $H_2$  or vibrationally excited  $H_2^v$ , respectively) for the collinear  $H+H_2$  reaction. The dashed lines are for the vibrationally unexcited reactant and are computed assuming either vibrational adiabaticity (VA) or conservation of vibrational energy (CVE) as discussed in the text. In each case the potential energy barrier as a function of distance,  $s$ , from the saddle point is shown in the accompanying insert. The  $T$  at  $E=0.794$  eV indicates the position of the threshold for vibrational excitation. The circles (ground vibrational state) and the square (excited vibrational state) are the reaction probabilities calculated by Mortensen and Pitzer for an LEPS potential energy surface. These circles and the square have been shifted to the right by 0.076 eV (the difference in classical barrier heights of their potential surface and the one used here). The solid and dotted curves are results of the present exact calculations.

them,<sup>21</sup> and computed a unitary  $S$  matrix. This procedure gave more accurate results for the same step size  $h$  (distance between neighboring mesh points) than Diestler and McKoy's analysis procedure. The calculations are performed at each energy using 1156–5625 mesh points corresponding to different  $h$ . The transition probabilities from two or more such calculations were extrapolated<sup>22</sup> to  $h^2=0$ . The results, shown in Fig. 1, are believed to be accurate within about 1%. They are compared with an exact scattering calculation (using the FDBVM<sup>19</sup>) for the "classical" one-dimensional barrier  $V_c(s)$ , where  $s$  is the reaction coordinate<sup>23,24</sup> in normal mode coordinate space in which the reduced mass is the same in all directions.<sup>17</sup> The  $V_c(s)$  model is commonly used<sup>25</sup> for tunneling calculations; it assumes conservation of vibrational energy. Figure 1 shows it is in poor agreement with the exact calculations.

There has been much interest recently in vibrationally adiabatic theories of reaction.<sup>26–33</sup> For each point along the reaction path we computed the second derivative of the potential energy in the direction perpendicular in normal mode space to the reaction path. From this we computed as a function of  $s$  the zero point energy of the vibrational mode which becomes the symmetric stretch of the saddle point. Adding this to  $V_c(s)$  yields an approximate effective one-dimensional barrier  $V_a(s)$  for vibrationally adiabatic (VA) reactions. This barrier is 0.274 eV high. We computed exact transmission probabilities for this barrier by the FDBVM. Figure 1 shows that this treatment is much better than the conservation-of-vibrational-energy one for translational energies below 0.6 eV. This is the most

direct quantum mechanical test of the VA model ever made. The deviation of the VA transmission function from the exact one is due to its neglect of "centrifugal effects" associated with the curvature of the reaction path<sup>24,26,28,33</sup> and to vibrational nonadiabaticity.

Consideration of the final vibrational states of a collision is a less stringent test for the VA model than comparison of transmission probabilities at given energies. The VA model assumes conservation of vibrational quantum number occurs with probability 1.0. At energies for which two vibrational states of the reactant or product are energetically accessible and  $E_0$  is great enough to surmount the barrier, the statistical phase space theory<sup>34–36</sup> predicts this occurs with probability 0.5. Figure 1 shows that it occurs with probability about 0.55 for  $E_0=0.6-0.85$  eV. By detailed balance<sup>37,11,14</sup> the same probability of a nonadiabatic transition holds for collisions of vibrationally excited molecules with initial relative translational energies 0.08–0.33 eV. For either initial state, the calculations show appreciable probability of reaction into each of the four open channels in this total energy range. Thus the VA model is worse at higher energies.

Our results are similar to those of Mortensen and Pitzer<sup>9</sup> for a different potential surface.

We are grateful to Dr. Nicholas, W. Winter, and Dr. Isaiah Shavitt for discussions.

\* Research supported in part by the U.S. Atomic Energy Commission, Report Code CALT-767P4-58.

† Present address: Department of Chemistry, University of Minnesota, Minneapolis, Minn. 55455.

‡ Contribution 3993.

<sup>1</sup> K. J. Laidler and J. C. Polanyi, *Progr. Reaction Kinetics* **3**, 1 (1965).

- <sup>2</sup> H. S. Johnston, *Gas Phase Reaction Rate Theory* (Ronald Press Co., New York, 1966).
- <sup>3</sup> D. L. Bunker, *Theory of Elementary Gas Reaction Rates* (Pergamon Press Ltd., Oxford, England, 1966).
- <sup>4</sup> F. Kaufman, *Ann. Rev. Phys. Chem.* **20**, 45 (1969).
- <sup>5</sup> J. Hirschfelder, H. Eyring, and B. Topley, *J. Chem. Phys.* **4**, 170 (1936).
- <sup>6</sup> F. T. Wall, L. A. Hiller, and J. Mazur, *J. Chem. Phys.* **29**, 255 (1958).
- <sup>7</sup> F. T. Wall and R. N. Porter, *J. Chem. Phys.* **39**, 3112 (1963).
- <sup>8</sup> M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.* **43**, 3259 (1965), Sec. III.a.
- <sup>9</sup> E. M. Mortensen and K. S. Pitzer, *Chem. Soc. (London), Spec. Publ.* **16**, 57 (1962).
- <sup>10</sup> H. Pelzer and E. Wigner, *Z. Physik. Chem.* **B15**, 445 (1932).
- <sup>11</sup> E. M. Mortensen, *J. Chem. Phys.* **48**, 4029 (1968).
- <sup>12</sup> K. T. Tang, B. Kleinman, and M. Karplus, *J. Chem. Phys.* **50**, 1119 (1969).
- <sup>13</sup> C. C. Rankin and J. C. Light, *J. Chem. Phys.* **51**, 1701 (1969).
- <sup>14</sup> D. J. Diestler and V. McKoy, *J. Chem. Phys.* **48**, 2951 (1968).
- <sup>15</sup> D. J. Diestler, *J. Chem. Phys.* **50**, 4746 (1969).
- <sup>16</sup> F. Wall and R. N. Porter, *J. Chem. Phys.* **36**, 3256 (1962).
- <sup>17</sup> I. Shavitt, *J. Chem. Phys.* **49**, 4048 (1968).
- <sup>18</sup> I. Shavitt, R. M. Stevens, F. L. Minn, and M. Karplus, *J. Chem. Phys.* **48**, 2700 (1968).
- <sup>19</sup> D. G. Truhlar, Ph.D. thesis, California Institute of Technology, Pasadena, Calif., 1969.
- <sup>20</sup> S. Geltman, *Topics in Atomic Collision Theory* (Academic Press Inc., New York, 1969), p. 129.
- <sup>21</sup> L. M. Delves, *Nucl. Phys.* **26**, 136 (1961).
- <sup>22</sup> L. F. Richardson, *Phil. Trans. Roy. Soc. (London)* **A226**, 299 (1927); M. R. Osborne, *Quart. J. Mech. Appl. Math.* **13**, 156 (1960).
- <sup>23</sup> S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Co., New York, 1941), p. 97.
- <sup>24</sup> R. A. Marcus, *J. Chem. Phys.* **45**, 4493, 4500 (1966).
- <sup>25</sup> See, e.g., I. Shavitt, *J. Chem. Phys.* **31**, 1359 (1959); H. S. Johnston, *Advan. Chem. Phys.* **3**, 131 (1961); F. Klein, A. Persky, and R. E. Weston, *J. Chem. Phys.* **41**, 1799 (1964).
- <sup>26</sup> R. A. Marcus, *J. Chem. Phys.* **41**, 610 (1964).
- <sup>27</sup> R. A. Marcus, *J. Chem. Phys.* **43**, 1598 (1965).
- <sup>28</sup> R. A. Marcus, *J. Chem. Phys.* **45**, 2138 (1966); **46**, 959 (1967); *Discussions Faraday Soc.* **44**, 7 (1968).
- <sup>29</sup> R. A. Marcus, in *Chemische Elementarprozesse*, H. Hartmann, Ed. (Springer-Verlag, Berlin, 1968), p. 23.
- <sup>30</sup> R. A. Marcus, *J. Chem. Phys.* **49**, 2617 (1968).
- <sup>31</sup> M. S. Child, *Proc. Roy. Soc. (London)* **A292**, 272 (1966); *Mol. Phys.* **12**, 401 (1967); *Discussions Faraday Soc.* **44**, 68 (1968).
- <sup>32</sup> D. L. Bunker and T.-S. Chang, *J. Phys. Chem.* **73**, 943 (1969).
- <sup>33</sup> R. E. Wyatt, *J. Chem. Phys.* **51**, 3489 (1969).
- <sup>34</sup> P. Pechukas and J. C. Light, *J. Chem. Phys.* **42**, 3281 (1965).
- <sup>35</sup> E. E. Nikitin, *Teor. Eksp. Khim.* **1**, 135, 428 (1965) [English transl.: *Theor. Exptl. Chem.* **1**, 83, 275 (1965)].
- <sup>36</sup> J. Lin and J. C. Light, *J. Chem. Phys.* **45**, 2545 (1966).
- <sup>37</sup> L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Nonrelativistic Theory* (Pergamon Press Ltd., Oxford, 1965), 2nd ed., Sec. 141.

## Evidence for the Dry Charge Pair in the Radiolysis of Water

TAKESHI SAWAI

*Tokyo Metropolitan Isotope Research Center, Setagaya, Tokyo*

AND

WILLIAM H. HAMILL

*Department of Chemistry and the Radiation Laboratory,\* University of Notre Dame, Notre Dame, Indiana 46556*

(Received 22 December 1969)

The dry hole in water ( $\text{H}_2\text{O}^+$  or  $\text{H}_3\text{O}^+$ , not hydrated) can be expected to undergo trapping by anions at high

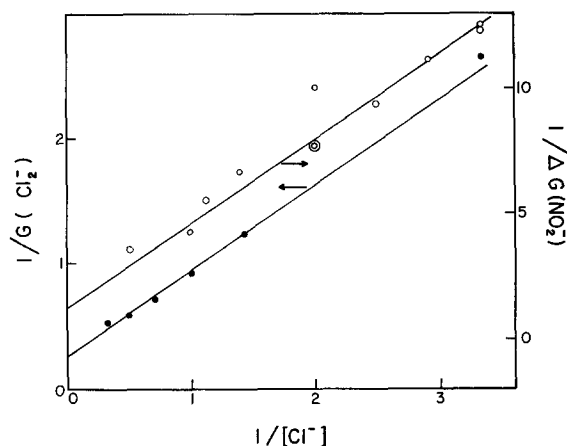
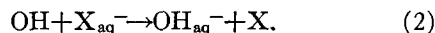
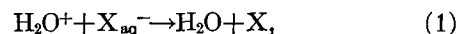


FIG. 1. The increase in  $G(\text{NO}_2^-)$  from  $10^{-2}M$   $\text{KNO}_3$  attributed to  $\Delta G(e_{aq}^-)$  due to hole trapping by  $\text{Cl}_{aq}^-$ . The  $\text{Cl}_2^-$  is a consequence of hole trapping by  $\text{Cl}_{aq}^-$  (From the data of Anbar and Thomas, Ref. 2).

concentrations. It will be difficult to distinguish this mechanism (1) from simple oxidation by OH, mechanism (2), for  $\text{I}_{aq}^-$  and other reactive species:



The distinction is straightforward using  $\text{Cl}_{aq}^-$  as the hole trap because it cannot be oxidized by OH in neutral solution. The recombination energies of  $\text{H}_2\text{O}^+$  and  $\text{H}_3\text{O}^+$  are  $\sim 12$  eV and  $\sim 6.5$  eV, respectively, while the long-wavelength limit of the  $\text{Cl}_{aq}^-$  spectrum sets the electron photodetachment energy at 6.7 eV, and at least one of the positive ion species will be reactive. The hole will be represented arbitrarily by the symbol  $\text{H}_2\text{O}^+$  hereafter.

Some prompt recombination of the dry  $\text{H}_2\text{O}^+ - e^-$  pair is expected because the 100-eV yield of  $e_{aq}^-$  is only 2.7. Also, Mozumder<sup>1</sup> has shown by theoretical considerations that most of the fast neutralization in water involves the dry charge pair. Consequently, hole annihilation by  $\text{X}^-$  should facilitate  $e^- \rightarrow e_{aq}^-$ , with an observable increase in  $G(e_{aq}^-)$ .

In the relevant time range  $< 10^{-11}$  sec there is no molecular diffusion and conventional kinetics do not apply, i.e.,  $k[\text{H}_2\text{O}^+][\text{S}]$  for some solute S is not defined. If the alternative to hole trapping by S is hydration and recombination, then we may adopt a trial function  $\sigma_1[\text{S}]/\sigma_{11}$  to describe the relative probabilities of trapping and either or both of the "first-order" processes. To be useful this description requires only the invariance  $\sigma_1/\sigma_{11}$  over the range of  $[\text{S}]$ , with  $\sigma_1$  being a probability per unit time at unit number density of S and  $\sigma_{11}$  the probability of first-order processes. This assumption gives a function of familiar algebraic form,

$$G(\text{product}) = G_1^0(\text{product}) \pm \frac{G_2^0(\text{precursor})\sigma_1[\text{S}]}{\sigma_1[\text{S}] + \sigma_{11}}. \quad (3)$$