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Rotational Relaxation of Molecular Hydrogen at Moderate Temperatures

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Using a coupled rotation-vibration-dissociation model[1] the rotational relaxation times for molecular hydrogen as a function of final temperature (500–5000 K), in a hypothetical scenario of sudden compression, are computed. The theoretical model is based on a master equation solver. The bound-bound and bound-free transition rates have been computed using a quasiclassical trajectory method.[1] A review of the available experimental data on the rotational relaxation of hydrogen is presented, with a critical overview of the method of measurements and data reduction, including the sources of errors. These experimental data are then compared with the computed results.

Nomenclature

D_0 = dissociation energy
$\langle e_R \rangle$ = average rotational energy per molecule, cm^{-1}
$\langle e_v \rangle$ = average vibrational energy per molecule, cm^{-1}
$G(v, J)$ = energy of the vibrational-rotational level v, J measured with from the $v = 0$ level
h = Planck's constant
$K(v; c)$ = transition rate coefficient for $v \rightarrow c$ (continuum) transition, $\text{cm}^3\ \text{s}^{-1}$
$K(v, J; c)$ = transition rate coefficient for $v, J \rightarrow c$ (continuum) transition, $\text{cm}^3\ \text{s}^{-1}$
$K(v, J; v', J')$ = transition rate coefficient for $v, J \rightarrow v'$, J' transition, in $\text{cm}^3\ \text{s}^{-1}$
$K(v; v')$ = transition rate coefficient for $v \rightarrow v'$ transition, $\text{cm}^3\ \text{s}^{-1}$
k = Boltzmann constant
N = number density
n = temperature exponent in rate coefficient
p = pressure in atmosphere
Q_J = partition function for rotational level J
Q_{tA}, Q_{tB} = translational partition function for atoms A and B, respectively
Q_v = partition function for vibrational level v
T = translational temperature
T_a = geometrical mean temperature
T_d = characteristic temperature of dissociation
T_v = vibrational temperature
t = time, s
θ = characteristic vibrational temperature for $H_2 = [E(1) - E(0)]/k = 6320\ \text{K}$
ρ_A, ρ_B = normalized population density of atoms A and B, respectively
ρ_v = normalized population density at vibrational level v
ρ_v, J = normalized population density at rotational level J of the vibrational level v
τ_L = relaxation time deduced from the Landau-Teller equation
$\langle\ \rangle$ = average value

Subscripts
A = atoms A
B = atoms B
E = equilibrium
i = initial condition
J = rotational level J
R = rotational
t = translational
v = vibrational level v, vibrational
x = molecule
0 = stagnation condition

I. Introduction

IN a recent publication[1] we reported the results of a theoretical study of the coupled rotation-vibration-dissociation phenomena in H_2. The study of the relaxation phenomena was conducted for two typical scenarios: 1) sudden compression and 2) sudden expansion. In both of these cases, a constant volume, isothermal condition was assumed. Computations were also conducted for a rotationless approximation similar to Ref. 2. The analysis showed that rotation plays a very important role in the relaxation of molecular hydrogen. It was found that during relaxation, in both the cooling and heating environments, a fraction of vibrational energy is transferred to the rotational states, and near equilibrium, it is transferred back to the vibrational levels. This process seems to delay the dissociation process. At higher rotational levels of lower vibrational states, where the rotational energy constitutes a good fraction of the total energy, the molecule relaxes faster as compared to the rotationless approximation. Overall effect of the rotation seems to be that it stretches the relaxation process a bit longer. The analysis also revealed a long incubation period prior to the actual relaxation. Existence of such an incubation period in CO has been experimentally demonstrated by Appleton et al.[3]

Rotation can change vibrational transition rates in two different ways. First, it changes the shape of the vibration potential. In the high-temperature range, the majority of the molecules are at a high rotational quantum number. When the rotational motion is excited to this extent, the effective interactive potential is shifted upward, reducing the effective dissociation energy and producing a rotational barrier. Both the vibrational bound-bound and vibrational bound-free transition rates are affected by this. The second rotational effect involves rotational energy transfer providing an additional pool of energy.

As the effects of the rotational degree of freedom (DOF) on the relaxation process are being studied using the model, it becomes imperative that this theoretical model be validated

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against available experimental data. Since most experimental data are in the form of rotational relaxation times or number of collisions required to achieve the rotational equilibrium, for the purpose of comparison, the rotational relaxation times as a function of temperature are computed. In this article, the results of such computations, for a hypothetical scenario of sudden compression, are presented. The final temperature resulting from the sudden compression is varied from 500 to 5000 K. Next, the available experimental data on rotational relaxation of molecular hydrogen are reviewed, including the methods of measurements, data reduction, and sources of errors involved. Finally, we compare these experimental data with the computed results.

II. Theoretical Model

A. Quasiclassical Trajectory Method

The theoretical model is described in detail in Ref. 1. However, for completeness, a brief outline of the procedure will be given here. The model considers only the processes involving molecule-to-molecule collisions. The state-to-state rate coefficients for this study have been determined using a quasiclassical trajectory method. This requires as input a potential energy function[4] which describes the interaction of the two hydrogen molecules. The potential used in the present work is a multiparameter analytic representation of the results of extensive ab initio electronic structure calculations, and is expected to faithfully reflect the properties of the accurate potential.

The initial conditions for the trajectories were selected as in Ref. 4, with the exception that for each temperature one maximum impact parameter was used. For 800, 1000, 3000, 5000, and 10,000 K, the impact parameters used were 15, 12, 10, 10, and $8a_0$ ($1a_0 = 5.291771 \times 10^{-9}$ cm), respectively. The initial states were fixed in all these computations. The initial state for the target was one of the 348 levels, and the initial state for the projectile was taken as the most likely state from a thermal distribution consisting only of molecules having J even(odd) if the target J was odd(even).

The final states of the target were assigned using the histogram method while a summation over the final states of the projectile were performed. This yields rates for all processes of the form

$$\mathrm{H}_2(v, J) + M \rightarrow \mathrm{H}_2(v', J') + M \tag{1}$$

$$\mathrm{H}_2(v, J) + M \rightarrow \mathrm{H} + \mathrm{H} + M \tag{2}$$

This determines all state-to-state rate coefficients except the ones for free-to-bound transitions. These are generated from the bound-to-free transition rate coefficients by using microscopic reversibility. Finally, to ensure that the proper equilibrium is reached, all bound-bound state-to-state rate coefficients for endoergic transitions are replaced with the values calculated using microscopic reversibility from the reverse transitions.

B. Formulation of Rate Equations

We will designate the H_2 molecule with the suffix x, and the two atoms resulting from its dissociation by the suffices A and B, even though they are identical. We consider that the mixture containing the species x, A, and B is confined in a box of unit volume. At times prior to $t = 0$, equilibrium existed at a specified temperature T_0. At time $t = 0$, the gas is suddenly heated by an unspecified means so that the translational temperature acquires a new value T. The box is henceforth maintained at an isothermal condition. Due to the suddenly changed T, collisional processes occur to vibrationally excite or de-excite to relax to a condition appropriate to T. Some of the collisions lead to a free-bound (dissociation or recombination) transition $v, J \rightleftharpoons A + B$. The state $A + B$ will be designated by c (continuum). There are a total of 15 vibrational states starting from $v = 0$ to $v = 14$, and a total of 348 rotational states with 39 rotational states at $v = 0$ and 5 rotational states at $v = 14$. It is further assumed that the ionization level is small and the bound-bound collisional transitions occur only when both colliding partners are molecules.

The quasiclassical trajectory calculations yield a set of transition rate coefficients among all combinations of initial and final rotational and vibrational, and/or free states. The master equations are written in the following form:

$$\frac{1}{N_x}\frac{\partial \rho_{v,J}}{\partial t} = \sum_{v}\sum_{J} K(v, J; v', J')(\rho_{v',J'} - \rho_{v,J})$$

$$+ K(v, J; c)(\rho_A\rho_B - \rho_{v,J})$$

$$\rho_{v,J} = \frac{N_{v,J}}{N_{(v,J)E}}, \quad \rho_A = \frac{N_A}{N_{AE}}, \quad \rho_B = \frac{N_B}{N_{BE}} \tag{3}$$

where $\rho_{v,J}$, ρ_A, and ρ_B are all normalized with respect to their equilibrium value. $K(v, J; v', J')$ is the transition rate coefficient for the transition $(v, J) \rightarrow (v', J')$ given in the units of cm^3 s^{-1}. Similarly $K(v, J; c)$ is the rate coefficient for the transition from bound-to-free state. N_x is the number of colliding molecules. The equilibrium number densities of the free state, N_{AE} and N_{BE} are given by

$$\frac{N_{AE}N_{BE}}{N_x} = \frac{Q_{At}Q_{Bt}}{Q_{xt}Q_x}\exp\left(-\frac{D_0}{kT}\right) \tag{4}$$

Here, Q denotes a partition function, and the subscripts t, x, A, and B refer to the translational mode, molecules, atoms A and atoms B, respectively. We invoke the principle of detailed balancing between a forward and its backward rates under equilibrium, which leads to

$$K(v, J; v', J')N_{(v,J)E} = K(v', J'; v, J)N_{(v',J')E}$$

$$K(v, J; c)N_{(v,J)E} = K(c; v, J)N_{AE}N_{BE}$$

The rate of change of the density of the atoms A and B and of the molecular density can be expressed as

$$\frac{\partial(\rho_A\rho_B)}{\partial t} = 2\sqrt{\frac{\rho_A\rho_B}{(N_AN_B)_E}}\sum_{v}\sum_{J} K(v, J; c)N_xN_{(v,J)E}$$

$$\times\ (\rho_{v,J} - \rho_A\rho_B) \tag{5}$$

The 348 equations from Eqs. (3) and (5) must be integrated numerically to obtain $\rho_{v,J}$ and $\rho_A\rho_B$ as functions of time.

The integration of the master equations yield the normalized population distribution of all rotational and vibrational states as a function of time as well as the number densities of the atoms and molecules. From these rotational and vibrational distributions, various quantities of interest such as the average vibrational energy $\langle e_v \rangle$, average rotational energy $\langle e_R \rangle$, and the average combined vibrational-rotational energy $\langle e_{vR} \rangle$ are calculated.

C. Rotational Relaxation Time

In general, the rotational relaxation times can be computed by monitoring the time evolution of $\rho_{v,J}$, for a given vibrational and rotational quanta. However, in order to visualize the bulk rotational relaxation behavior, the quantity usually measured in an experiment, we follow the time evolution of the average rotational energy of the molecules. The average rotational energy is computed as follows:

$$e_R = \frac{\sum_{v=0}^{V_{\max}}\sum_{J=0}^{J_{\max}}[G(v, J) - G(v, 0)]N_{(v,J)E}\rho_{(v,J)}}{\sum_{v=0}^{V_{\max}}\sum_{J=0}^{J_{\max}}N_{(v,J)E}\rho_{(v,J)}} \tag{6}$$

where $G(v, J)$ is the vibrational rotational energy for a given v and J.

D. Dissociation Incubation Time

The incubation period is determined as the period for which the atomic population remains constant, i.e., $\partial N_{A,B}/\partial t \sim 0$.

III. Computational Strategy

In order to determine the transition rates, about 2000 trajectories, for each of the 348 levels, were integrated using the variable step-size algorithm.[1] Approximately one-tenth of the trajectories were back-integrated to monitor the suitability of the numerical parameters controlling the accuracy of the solutions. Most of the trajectories were evaluated using a Cray Y-MP, and 2000 trajectories required from 15 min (T = 10,000 K) to 70 min (T = 800 K) of CPU time. The transition rates for four temperatures, 10,000, 5000, 3000, and 1000 K, were computed during the work related with Ref. 1. A new set of rates for T = 800 K were computed during this investigation and the complete solution for this temperature took about 406 h on the Y-MP. Because of CPU time constraints, transition rates for other temperatures were not computed. Instead, the data for other temperatures were either extrapolated or interpolated from the available five sets of data.

Ideally, in order to determine the relative rotational populations, 348 simultaneous equations need to be solved. However, since solving 348 stiff equations can be very time consuming, a set of equally spaced 94 of these equations were selected and simultaneously solved. After a few time steps the population densities for all the 348 bound are updated by interpolation. A typical solution requires about 5.5 h on Cray Y-MP computer. A total of 10 cases, in the 500–5000 K range, were solved. The transition rates for these 10 cases were obtained by interpolating or extrapolating the tables obtained for the original five temperatures.

IV. Reveiw of Available Experimental Data

Experimental data[5–9] considered (except for Gallagher's[7]), are primarily from shock tubes studies. Beside being able to acquire the relaxation data over a wide range of temperatures, shock tube measurements are more direct as far as the relaxation times are concerned. Although shock tubes are excellent impulse facilities in simulating gas compression, the flow of gases in the tubes exhibits "nonideal" behavior. The boundary-layer growth along the wall behind the shock front induces gasdynamic nonuniformities: 1) the density behind the shock is no longer constant; and 2) as a result of the boundary layer, the shock front becomes curved. So in contrast to an ideal shock tube flow, the real flow becomes two-dimensional and time-dependent. The perturbations increase with the distance from the shock front and obscure the relaxation process, especially in integrated density measurements, which are the basis of most relaxation time measurements. Thus, for a critical interpretation of density measurements in the relaxation regions, the boundary layer influence must be taken into account. Lensch and Gronig[6] have discussed in detail these boundary-layer effects and corrected their experimental data accordingly. Yoder[9] and Boitnott et al.[5] have presented their data without any such corrections. Gallagher and Fenn[7] used so-called "heat capacity lags" by time of flight (TOF) analysis of moleculer beams extracted from free jets. They extracted a beam at several distances from a nozzle exit and determined the axial variation of translational temperature. With the help of an energy balance, assuming negligible vibrational energy, and some independent measurements of axial flux density in the jet, they obtained the rotational temperature T_R.

At low temperatures (≈500 K), most of the internal energy of hydrogen remains in the rotational DOF. As the temperature increases, the molecules become vibrationally excited and eventually dissociate. The dissociation, however, is preceded by a period of incubation, since a finite time is necessary for molecules to be vibrationally excited before they can dissociate. For CO molecule, this incubation period, as measured by Appleton,[3] was found to be one to two orders of magnitude higher than that predicted by the Millikan and White formula based on the Landau-Teller formulation. Data on the incubation period for hydrogen molecules are not available at present time.

V. Results

As mentioned above, the transition rates for five different translational temperatures, namely, for T = 800, 1000, 3000, 5000, and 10,000 K, were computed. Some selected transition rates, $K(v, J; v', J')$, as functions of temperature are shown in Fig. 1. As can be seen from the figure, the transition rates show monotonic variation (decrement or increment) over the 800–10,000 K temperature range, and for a given temperature one should be able to estimate the appropriate rate by way of interpolation with reasonable accuracy. On the other hand, the estimates for a temperature lower than 800 K can be made by extrapolation, provided the temperature dependence of the rates does not dramatically change over this range. Extrapolated values for T = 500 K have also been plotted in Fig. 1.

In Fig. 2, the average rotational energy is plotted as a function of time for the sudden compression scenario T = 400 → 500. We can see the exponential nature of the relaxation phenomena as normally recorded in the experiments.

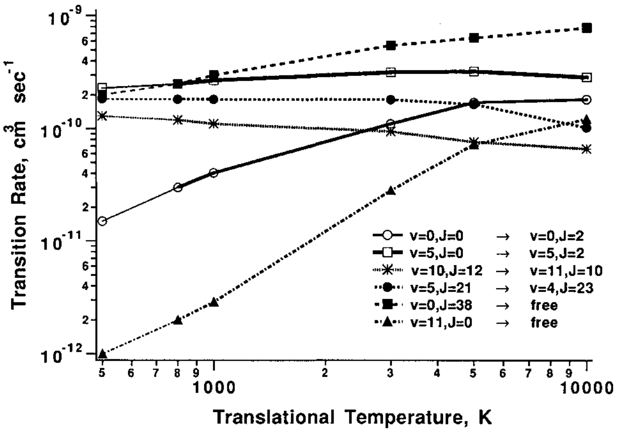

Fig. 1 Bound-bound and bound-free transition rates as functions of time.

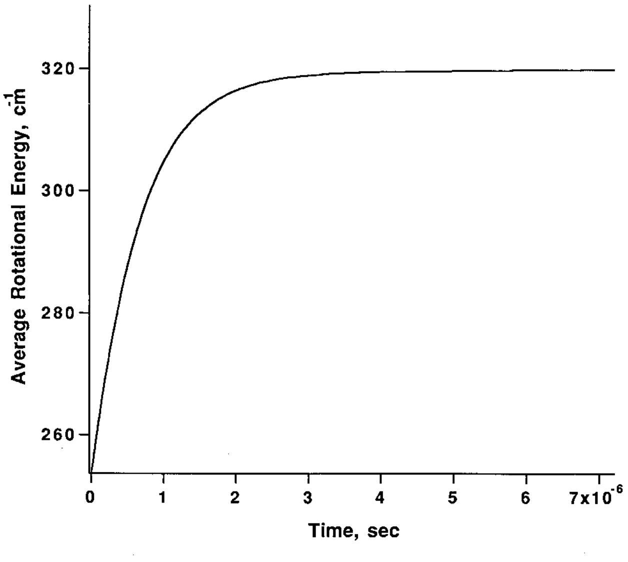

Fig. 2 Average rotational energy as a function of time. T = 400 → 500 K.

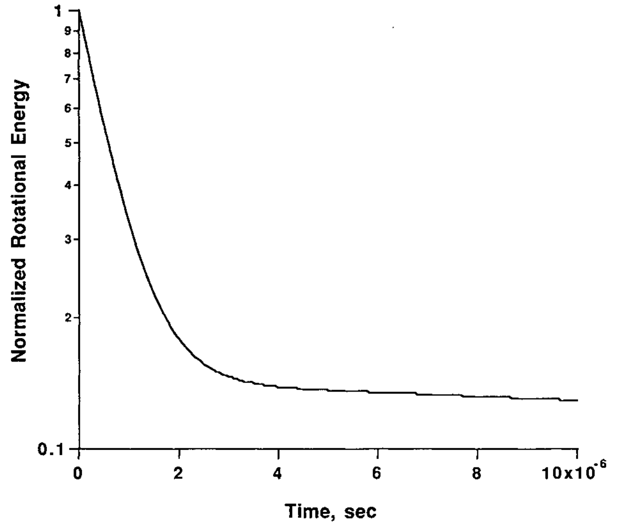

Fig. 3 Normalized rotational energy as a function of time. T = 400 → 500 K.

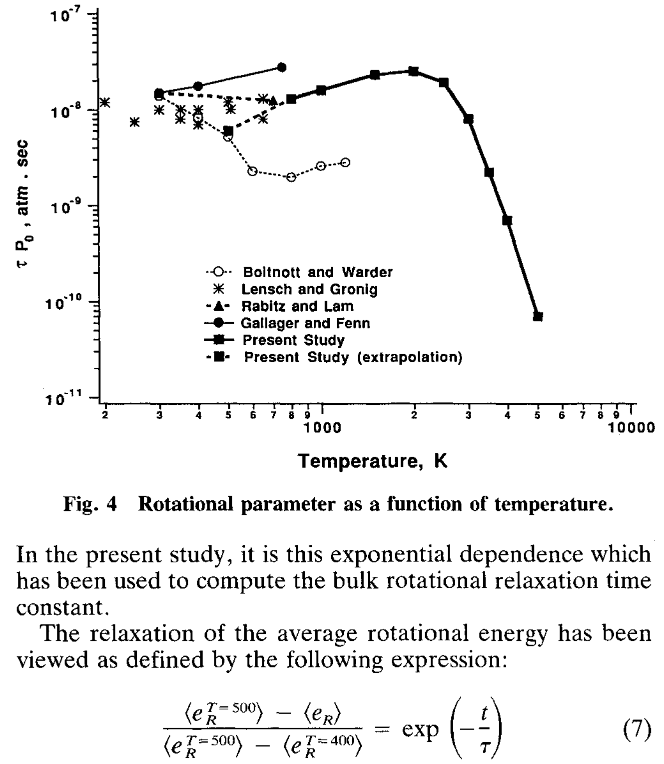

Fig. 4 Rotational parameter as a function of temperature.

In the present study, it is this exponential dependence which has been used to compute the bulk rotational relaxation time constant.

The relaxation of the average rotational energy has been viewed as defined by the following expression:

$$\frac{\langle e_R^{T=500}\rangle - \langle e_R\rangle}{\langle e_R^{T=500}\rangle - \langle e_R^{T=400}\rangle} = \exp\left(-\frac{t}{\tau}\right) \tag{7}$$

In order to compute the relaxation time τ the average rotational energy is expressed in a nondimensional form [left side of Eq. (7)], and is plotted as a function of time (Fig. 3). The slope of this curve on a semilog plot is used to compute the relaxation time. Rotational relaxation times were computed for the following 10 cases: 1) $T = 400 \rightarrow 500$ K; 2) $T = 600 \rightarrow 800$ K; 3) $T = 800 \rightarrow 1000$ K; 4) $T = 1400 \rightarrow 1500$ K; 5) $T = 1800 \rightarrow 2000$ K; 6) $T = 2000 \rightarrow 2500$ K; 7) $T = 2800 \rightarrow 3000$ K; 8) $T = 3000 \rightarrow 3500$ K; 9) $T = 3000 \rightarrow 4000$ K; and 10) $T = 4000 \rightarrow 5000$ K.

The sudden compression was assumed to occur under constant volume and isothermal conditions. In all the cases, the predissociation total molecular number density N_0 was assumed to be 1.0×10^{17} cm^{-3}. The computed values of τp_0 in s/atm, where P_0 is the partial pressure of the molecular species at the given temperature, are plotted in Fig. 4 as functions of temperature. For comparison, the above-mentioned experimental data are also plotted in the figure. Since some of the data is published in terms of Z_r, number of collisions required to relax the rotational energy to within 1/e of its equilibrium value, they are converted to τp_0 in s/atm, assuming a reference collision cross section of 2.93 Å, based on Lennard-Jones potential for hydrogen.[7] Since Boitnott and Warder[5] used hard sphere cross sections from viscosity data and their values were very low, the latter were multiplied by a factor of two for comparison. Surprisingly, Boitnott's data are still the lowest for temperatures above 500 K. More disturbing than the disagreement in absolute magnitude is the fact that, for the 200–1200 K temperature range, Boitnott and Warder find $\tau \cdot P_0$ decreases with increasing temperature. All other data including Yoder's[9] and Lensch and Gronig's[6] show an increase in the relaxation parameter with increasing temperature in this range. The most logical explanation seems that Boitnott and Warder do not attempt to fit the observed density variation through the shock wave with a relationship obtained by solving the relaxation equation. Instead, they compared the measured shock wave thickness with one computed by assuming an exponential dependence of specific heat ratio variation and the thermodynamic expression for density increase through a normal shock. In this methodology, the accuracy of the deduced data depends upon the comparison of theory and experiment at one single point, downstream of the shock front. Also this point at which comparisons are made may be difficult to locate.

The computed data from this present study, marked with thick solid line with square symbols in Fig. 4, are in reasonable agreement with Lensch and Gronig's data. Although, the computed values at T = 500 K (dotted line with square symbols) are slightly lower than their data. It should be remembered that the cross sections for this temperature were obtained by extrapolation, instead of actual trajectory computations; extrapolations could be reponsible for this discrepancy. Gallagher and Fenn's[7] data are slightly higher, however, their general trend is the same as the computed data and Lensch and Gronig's[6] data. No reliable data are available for temperatures above 700 K.

For temperatures above 700 K and below 2000 K, the computations show that the rotational relaxation parameters, $\tau \cdot P_0$ continues to increase with increase in temperature. At around 2000 K, with 2% of the molecules dissociated, $\tau \cdot P_0$ achieves a maximum of 2.5×10^{-8} atm/s. At this point the dissociation starts to play an important role in the relaxation process. The energy lost in each dissociation is 36,110.8 cm^{-1} and it occurs at the expense of the energy in the rotational mode. As a result, the equilibration process of the rotational energy slows down. From Fig. 4 we can see that the relaxation parameter $\tau \cdot P_0$ decreases rapidly, as the temperature increases from

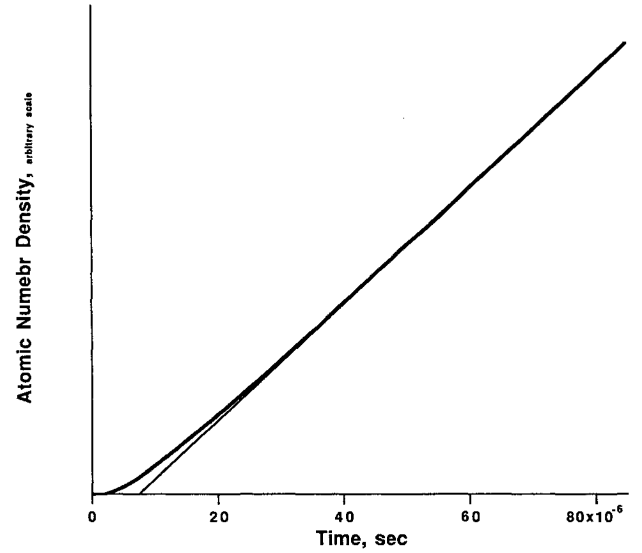

Fig. 5 Atomic number density as a function of time.

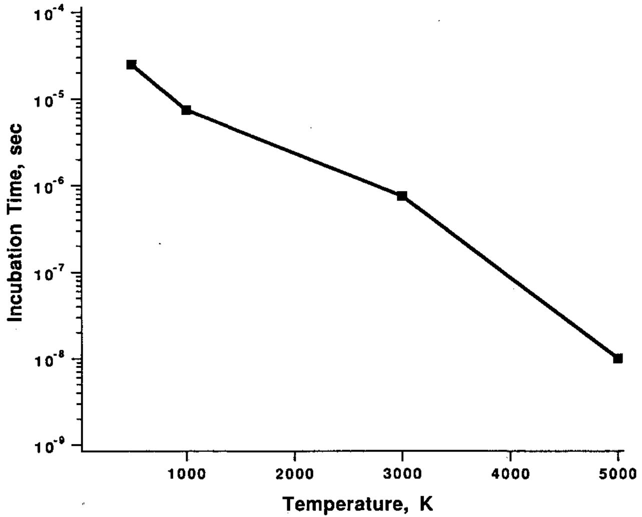

Fig. 6 Incubation time as a function of temperature.

2000 to 5000. At around 5000 K about 99% of the molecules are dissociated and the value of $\tau \cdot P_0$ decreases to 7×10^{-11} atm/s.

Atomic number density as a function of time, for the case $T = 2800 \rightarrow 3000$ K, is plotted in Fig. 5. The atomic population remains constant for a considerable period of time, indicating a distinct incubation period, and then starts to increase rapidly achieving a near-constant rate of increase. Finally, the rate of increase in the atomic number density (not shown in the figure) starts to drop, becoming negligible, when the atomic population almost achieves its equilibrium value. This incubation period has been computed for various temperatures and is plotted in Fig. 6. It has been found that at $T = 500$ K the incubation period is large, about 25 s. This period decreases rapidly with increase in temperature, as can be seen from the figure, dropping to about 0.01 s at $T = 5000$ K.

VI. Conclusions

Bound-bound and bound-free transition rates for H_2-H_2 collisions have been computed for five temperatures, namely, $T = 800$, 1000, 3000, 5000, and 10,000 K. Using these transition rates rotational relaxation parameter τp_0 have been computed. The computed values of the τp_0 are in good agreement with Lench and Gronig's[6] data. Incubation period for dissociation of hydrogen were also calculated.

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