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# COLLISION INDUCED VIBRATIONAL TRANSITIONS IN $H_2$ WITHIN THE BREATHING-SPHERE MODEL

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The breathing-sphere model has been employed to calculate cross sections for vibrational de-excitation of the $H_2$ molecule in collisions with an atom. From these cross sections the vibrational rate constants were computed and compared with experiment. Fairly good agreement is obtained between the theoretical rates and experimental values.

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## 1. *Introduction*

Within the past several years a number of various semiclassical and quantum approximations in the theoretical investigations of vibrational and ro-vibrational energy transfers in atom-molecule collisions have been developed (for a recent review see Ref. [1]). This interest in approximate methods is caused by the fact that performing scattering calculations within the rigorous quantum close-coupling (CC) method [2] is still a tremendous task. The computational effort increases so rapidly with the number of channels which must be included to obtain convergent results for vibrational and ro-vibrational transitions, that calculations within the CC treatment are practical only when a few internal ro-vibrational levels are energetically accessible. One of the previous attempts to simplify the computational work on pure vibrational transitions is the so-called breathing-sphere (BS) approximation [3].

In this work we performed BS calculations on the He—$H_2$ system for a few energies in the range 0.6–1.5 eV. In the next section we briefly outline the breathing-sphere model, the interaction potential and some computational procedures. The last section presents our results and compares them with experimental data.

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## 2. *Collision model and computational procedures*

### 2.1. Breathing-sphere equations

In the assumed collision model [3] the oscillating molecule is treated as a pulsating sphere interacting via a spherically-symmetric potential with an incoming atom. Therefore no rotational transitions will be induced by collisions. This collision system, after elimination of the center-of-mass motion, is described by the Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu}\Delta_{\boldsymbol{R}}-\frac{\hbar^2}{2m}\Delta_r+V_0(r)+V(R, r)\right]\psi(\boldsymbol{R}, r) = \psi(\boldsymbol{R}, r), \tag{1}$$

where $\boldsymbol{R}$ is the position vector of the incident atom relative to the center-of-mass of the molecule, $r$ is the vibrational variable, $V(R, r)$ is the scattering potential, $V_0(r)$ is the vibrational potential of the molecule, $m$ is the reduced mass of the molecule, and $\mu$ is the reduced mass of the atom-molecule system.

Since the interaction potential is spherically-symmetric a solution of Eq. (1) is sought in the form

$$\psi(\boldsymbol{R}, r) = \sum_n \frac{\chi_n(r)}{r}\psi_n(R, \theta), \tag{2}$$

where $\chi_n(r)$ are solutions to the vibrational equation for the isolated molecule

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+V_0(r)-\varepsilon_n\right]\chi_n(r) = 0. \tag{3}$$

A partial-wave analysis can be introduced by expanding $\psi_u(R, \theta)$ in terms of Legendre polynomials

$$\psi_n(R, \theta) = \sum_l \frac{F_n^l(R)}{R}P_l(\cos\theta). \tag{4}$$

The radial functions $F_n^l(R)$ satisfy the set of coupled equations

$$\left[\frac{d^2}{dR^2}+k_n^2-\frac{l(l+1)}{R^2}\right]F_n^l(R) = \frac{2\mu}{\hbar^2}\sum_{n'}\langle n|V(R, r)|n'\rangle F_{n'}^l(R), \tag{5}$$

where

$$k_n^2 = \frac{2\mu}{\hbar^2}(E-\varepsilon_n), \tag{6}$$

and the coupling matrix elements are defined by

$$\langle n|V(R, r)|n'\rangle = \int_0^\infty \chi_n(r)V(R, r)\chi_{n'}(r)dr. \tag{7}$$

The boundary conditions imposed on the scattering problem require that the solution $F_n^l$ should be finite at the origin and should have the following asymptotic form for large $R$:

$$F_n^l(R) \underset{R\to\infty}{\sim} \delta_{nn'} \exp\left[-i(k_n R - l\pi/2)\right] - \left(\frac{k_n}{k_{n'}}\right)^{1/2} S_{nn'}^l \exp\left[i(k_{n'}R - l\pi/2)\right], \tag{8}$$

for open channels, and

$$F_n^l(R) \underset{R\to\infty}{\sim} 0, \tag{8'}$$

for closed channels.

As it is seen from Eq. (8) the asymptotic behavior of $F_n^l(R)$ defines the scattering matrix $\boldsymbol{S}$. All observable quantities can be computed from the $\boldsymbol{S}$ matrix. The differential cross section for vibrational excitation from level $n$ to $n'$ may be written as

$$\frac{d\sigma_{n\to n'}}{d\Omega} = \frac{1}{4k_n^2}\left|\sum_{l=0}^{\infty}(2l+1)\,(S_{nn'}^l - \delta_{nn'})P_l(\cos\theta)\right|^2, \tag{9}$$

and the total cross section is given by

$$\sigma_{n\to n'} = \sum_{l=0}^{\infty} \sigma_{n\to n'}^l, \tag{10}$$

where the partial cross sections $\sigma_{n\to n'}^l$ are defined by

$$\sigma_{n\to n'}^l = \frac{\pi}{k_n^2}(2l+1)\,|S_{nn'}^l - \delta_{nn'}|^2. \tag{11}$$

### 2.2. Coupling matrix elements

For the He—H$_2$ interaction $V(R, r)$ in Eq. (1) we have used the CI potential energy surface computed by Tsapline and Kutzelnigg [4] and complemented by Raczkowski and Lester [5]. The required spherically-symmetric part of this potential can be expressed in the analytical form (energies and distances are in atomic units)

$$\begin{aligned} V(R, r) = {} & (8.392 - 8.130x - 1.754x^2 + 3.882Rx)\exp(-1.933R) \\ & - s(R)\left(\frac{4.531 + 2.171x}{R^6} + \frac{60.062 + 155.42x}{R^8}\right), \end{aligned} \tag{12}$$

where $x = r - 1.406$ and the switching function $s(R)$ is defined by

$$s(R) = \tfrac{1}{2}\left[1 + \tanh(R - 4.78)\right]. \tag{13}$$

All parameters were determined by the least squares procedure, minimizing the root-mean-square (rms) deviation defined by

$$\Delta = \left[\frac{1}{N}\sum_i \left(\frac{V_i - \tilde{V}_i}{\tilde{V}_i}\right)^2\right]^{1/2}, \tag{14}$$

where $N$ is the number of points, $\tilde{V}_i$ the "ab initio" value and $V_i$ the fitted value of the potential. The percent rms deviation was minimized to 3%. With this choice of interaction potential the coupling matrix elements in Eq. (5) were calculated in terms of matrix elements over vibrational states of the type $\langle n|x|n'\rangle$ and $\langle n|x^2|n'\rangle$.

Vibrational eigenfunctions were obtained as solutions of Eq. (3) in which $V_0(r)$ was taken to be the accurate "ab initio" Kołos-Wolniewicz potential for the $X^1\Sigma_g^+$ state of $H_2$ including adiabatic corrections for nuclear motion [6]. The vibrational eigenproblem (3) was solved by using the well-known method of Cooley [7], which is based on the Numerov algorithm for a numerical solution of differential equations.

### 2.3. Solution of the coupled radial equations

The system of coupled differential equations (5) can be written in the matrix form

$$\left[\mathbf{1}\frac{d^2}{dR^2}+\boldsymbol{W}(R)\right]\boldsymbol{F}(R) = 0. \tag{15}$$

These equations were solved by using the algorithm developed by Gordon [8]. This method is based on an outward propagation of the solution $\boldsymbol{F}(R)$ through a series of intervals. Within each interval the original potential is expanded into a power series

$$\boldsymbol{W}(R) = \boldsymbol{W}(\bar{R})+(R-\bar{R})\left.\frac{d\boldsymbol{W}}{dR}\right|_{R\to\bar{R}}+\tfrac{1}{2}(R-\bar{R})^2\left.\frac{d^2\boldsymbol{W}}{dR^2}\right|_{R=\bar{R}}+\ldots, \tag{16}$$

where $\bar{R} = (R_i+R_{i+1})/2$. In successive intervals the solutions are subject to a unitary transformation $\boldsymbol{M}(R)$, which is constructed to diagonalize the coupling matrix at the center of each interval; that is,

$$\boldsymbol{M}_i^\dagger \boldsymbol{W}(\bar{R}_i)\boldsymbol{M}_i = \boldsymbol{W}^0(\bar{R}_i), \tag{17}$$

where $\boldsymbol{W}^0$ is a diagonal matrix.

Within a sufficiently small interval this procedure decouples the initial equations (15) into $N$ ordinary differential equations

$$\left[\mathbf{1}\frac{d^2}{dR^2}+\boldsymbol{U}(R)\right]\boldsymbol{G}(R) = 0, \tag{18}$$

where $\boldsymbol{U}(R)$ is the so-called reference potential, i.e. a diagonal transform of the coupling matrix (16), and $\boldsymbol{G}(R)$ is the transformed solutions.

If the reference potential is chosen to be linear in $R$

$$U_n(R) = W_n^0+p_n(R-\bar{R}), \tag{19}$$

where $p_n$ is a diagonal element of the transformed first derivative of the coupling matrix, the solution can be expressed analytically in terms of Airy functions. For the $n$-th channel one has

$$G_n(R) = a_n Ai[\alpha_n(R-\beta_n)]+b_n Bi[\alpha_n(R-\beta_n)], \tag{20}$$

where $\alpha_n = (p_n)^{1/3}$ and $\beta_n = -(W_n^0/p_n + \bar{R})$. The coefficients $a_n$ and $b_n$ are determined by the matching conditions on the boundaries of the intervals. The piecewise analytic solutions (20) and their derivatives are matched between adjacent intervals and in such manner a solution is propagated step-by-step into the asymptotic region where the $S$ matrix can be extracted. The advantage of this method in a multichannel problem is mainly due to the fact that with this method it is easy to adjust the integration step size to maintain the desired level of accuracy. The interval size is controlled and determined by the accuracy of the polynomial approximation (16) to the original potential and is independent of the wavelength of the channel, while in the ordinary numerical methods the step size is governed by the wavelength. Hence, the number of steps needed in an ordinary numerical integration is at least ten times greater.

## 3. *Results and discussion*

In this section we present results of the BS calculations for the de-excitation of the first vibrational state of $H_2$ at total energies ranging from 0.63 to 1.5 eV. The calculated individual partial cross sections for selected energies are shown in Fig. 1. To determine the total cross section one must sum the quantity $(2l+1)|S_{nn'}^l|^2$ over all values of the orbital angular momentum for which $|S_{nn'}^l|$ is non-negligible. In Table I we list the total BS cross sections $\sigma_{1\to 0}$ at six values of total energy: 0.63, 0.75, 0.9, 1.1, 1.3 and 1.5 eV. The obtained total cross sections are also plotted as a function of energy in Fig. 2. In order to compare

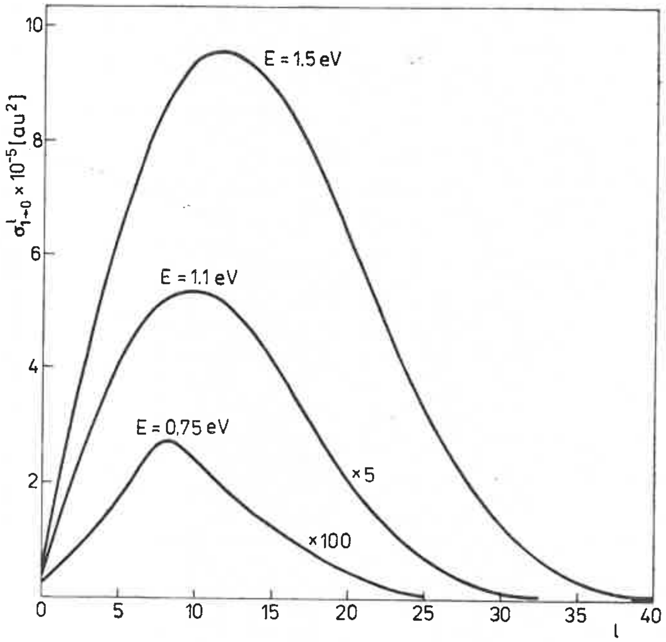

Fig. 1. Partial cross sections for vibrational transitions in $H_2$ induced by collisions with He

TABLE I

Breathing-sphere cross sections for the vibrational de-excitation of $H_2$ colliding with He

| $E$ [eV] | $\sigma_{1\to 0}$ [Å$^2$] | | | |
|---|---|---|---|---|
| | BS[a] | BS[b] | CC[c] | EP[d] |
| 0.63 | 0.1149 (−6) | — | — | — |
| 0.75 | 0.8779 (−6) | — | — | — |
| 0.90 | 0.7300 (−5) | 0.193 (−6) | 0.560 (−5) | 0.158 (−6) |
| 1.1 | 0.4830 (−4) | 0.684 (−5) | 0.308 (−4) | 0.104 (−4) |
| 1.3 | 0.1839 (−3) | 0.107 (−3) | 0.112 (−3) | 0.982 (−4) |
| 1.5 | 0.5155 (−3) | 0.743 (−3) | 0.294 (−3) | 0.390 (−3) |

[a] present calculations,
[b] breathing-sphere results from Ref. [11],
[c] close-coupling values of Raczkowski et al. [9],
[d] effective potential results of Rabitz and Zarur [11].

the present results with other theoretical calculations, we collected in Table I results obtained in the previous BS calculations of Rabitz and Zarur [11], as well as in the close-coupling (CC) method [9] and in the effective potential (EP) approach [11]. The only qualitative agreement of various theoretical results can be due to the fact that results reported in Table I were obtained by using both different interaction potentials and different collision schemes.

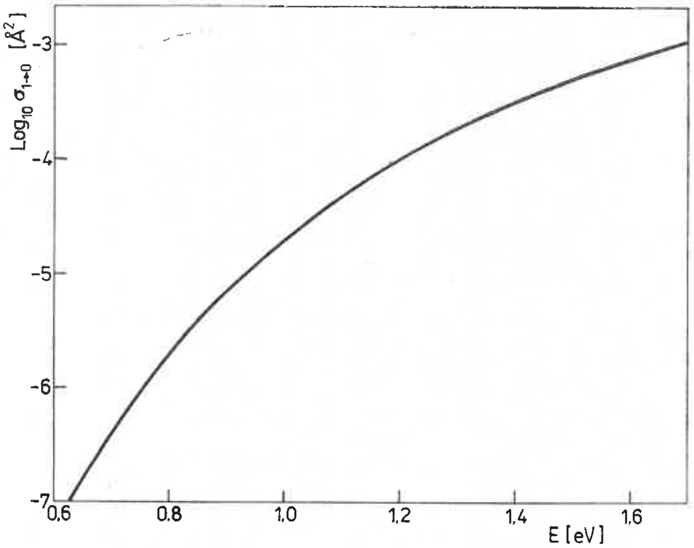

Fig. 2. De-excitation cross section for $H_2$ as a function of energy

Unfortunately, no direct comparison of theoretical cross sections with experimental data is possible, because experimental measurements of cross sections for collision induced vibrational transitions have not yet been carried out. However, extensive experimental investigations have been performed on vibrational relaxation processes, therefore experimental values of rate constants as well as relaxation times have been determined.

The transition rate constants for a process $n \rightarrow n'$ for a system in translational equilibrium at temperature $T$ are related to the calculated cross sections by averaging over the distribution of the relative velocities [12]

$$k_{nn'}(T) = \int_0^\infty v\sigma_{nn'}(v)f(v, T)dv, \tag{21}$$

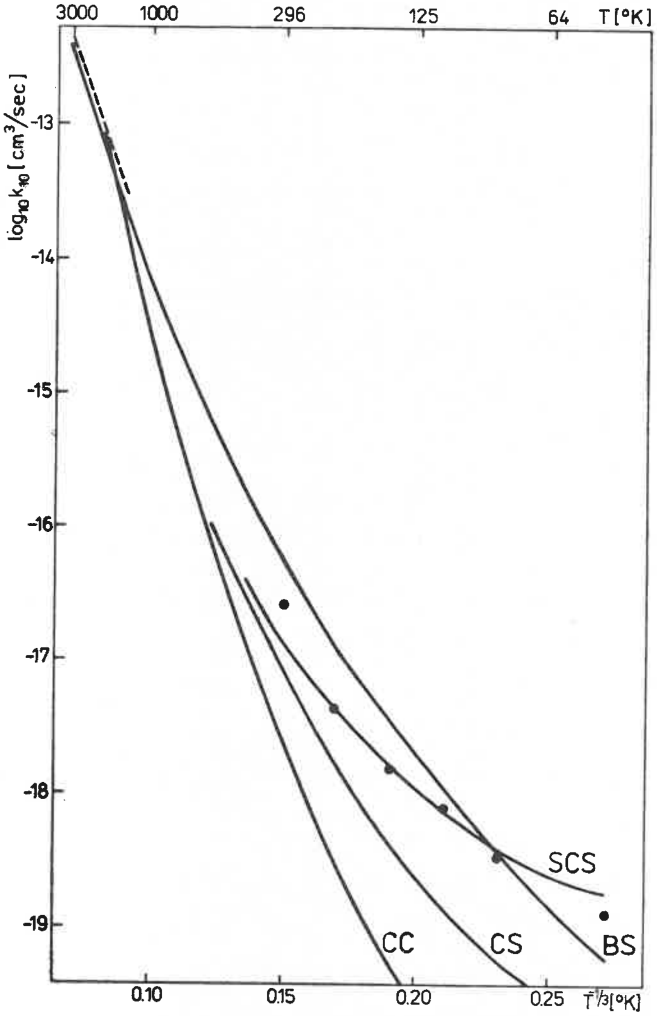

Fig. 3. The Landau–Teller diagram for theoretical and experimental rate constants for He—$H_2$ vibrational relaxation. The filled circles indicate the experimental points of Audibert et al. [13], the dashed line shows the results of Dove and Teitelbaum [14] and the solid lines refer to: BS — breathing-sphere calculations (present work), SCS — semiclassical computation of Billing [15], CS — coupled-states approximation [16], and CC — coupled channel results from Ref. [9]

where $f(v, T)$ is the three-dimensional Boltzmann distribution function

$$f(v, T) = 4\pi \left(\frac{\mu}{2\pi kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right). \tag{22}$$

If the relaxation process of a gas system is dominated by de-excitation from the first to the ground state, then the Landau–Teller model of relaxation could be assumed and the relaxation time is given by the two-level formula [12]

$$\tau^{-1} = k_{10} - k_{01}, \tag{23}$$

where $k_{01}$ and $k_{10}$ are the excitation and de-excitation rate constants respectively.

With the present BS cross section data from Table I, the de-excitation rates for the process $n = 1 \to n = 0$ were computed for $50 \leqslant T \leqslant 3000$ K. Fig. 3 compares our relaxation rates with other theoretical results, as well as with the experimental data of Audibert et al. [13] and Dove and Teitelbaum [14]. The comparison is shown in the standard Landau–Teller diagram (log $k_{nn'}$ versus $T^{-1/3}$). The rates determined from the BS cross sections are generally in satisfactory agreement with the experimental values from Refs. [13] and [14], except for the low temperature region, where the computed rates are too small. Theoretical errors could arise both from the choice of the potential surface and from the treatment of collision dynamics. Probably this discrepancy in the entire considered region of temperatures, arises from assuming elementary dynamics which does not include the rotational structure of the hydrogen molecule. The low temperature behavior of our results confirms the previous suggestion [10] that the vibrational relaxation is particularly affected by coupling with rotational motion at low temperatures. As can be seen from Fig. 3 the semiclassical (SCS) rates [15] are in better agreement with experiment than those from the coupled-states (CS) approximation [16] as well as from rigorous CC computation [9]. The CC studies of Raczkowski at al. [9] primarily explored the high temperature region ($T > 1000$ K), therefore their extrapolation to low temperatures are in doubt. Therefore further, accurate quantum computations are still desirable, especially at low temperatures. Nevertheless, the present work demonstrates that the BS model correctly predicts the essential features of the thermal vibrational relaxation. An important advantage of our approach is the large reduction in computer time required by the scattering part of these calculations. At the thermal energies of interest the number of coupled vibrational states to be considered is usually small enough so that the coupled equations could be economically solved, whereas in the conventional CC studies the resulting set of coupled equations is considerably larger.

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