SEMIEMPIRICAL ELECTRIC DIPOLE MOMENT AND ITS DERIVATIVE IN H₂-H₂ AND H₂-H COLLISIONS

by R. W. Patch

Lewis Research Center
Cleveland, Ohio 44135
The dipole moment and its derivative with respect to H₂ internuclear distance were calculated for intermolecular distances of 4 to 8 bohr (2.117×10⁻¹⁰ to 4.233×10⁻¹⁰ m) by using a semiempirical model for H₂-H₂ previously developed by others. In this model the dipole moment and its derivative are the sum of an overlap contribution and a quadrupole-induced contribution. For H₂-H₂ both contributions were improved. For H₂-H they were reformulated. For H₂-H₂ four planar configurations and one nonplanar configuration were used and substantial agreement with infrared absorption was obtained. For H₂-H three configurations were used. The ultimate application of the results is in calculating pressure-induced infrared absorption of hydrogen gas.
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SEMIEMPIRICAL ELECTRIC DIPOLE MOMENT AND ITS
derivative in H₂-H₂ and H₂-H collisions

by R. W. Patch
Lewis Research Center

SUMMARY

In a gas, when two H₂ molecules or an H₂ molecule and an H atom collide, a momentary electric dipole moment results. This electric dipole moment may cause pressure-induced infrared absorption. A knowledge of the strength of this absorption is necessary for radiant-heat-transfer calculations at high pressures. The strength depends, among other things, on the value of the electric dipole moment and its partial derivative with respect to H₂ internuclear distance. These quantities cannot be determined accurately from ab initio calculations on present day computers if the intermolecular distance is much greater than 4 bohr (2.117×10⁻¹⁰ m), nor can they be determined unambiguously from experiments.

In this report the electric dipole moment and its derivative for H₂-H₂ and H₂-H collisions were calculated for intermolecular distances of 4 to 8 bohr (2.117×10⁻¹⁰ to 4.233×10⁻¹⁰ m) by using a semiempirical model for H₂-H₂ previously developed by others. In this model the dipole moment and its derivative are the sum of an overlap contribution and a quadrupole-induced contribution. The quadrupole-induced contribution is analytically simple but requires correction of previously published expressions. The overlap contribution is analytically complicated. For H₂-H₂ the overlap analysis was improved, and for H₂-H it was reformulated. For both contributions the only experimental input was the equilibrium internuclear distance of H₂, which was obtained from spectroscopic data.

Dipole moment and its derivative were calculated for a number of collision configurations. For H₂-H₂ four planar configurations and one nonplanar configuration were used. For H₂-H three configurations were employed.

The semiempirical theory used in this report is not valid for intermolecular distances less than 4 bohr (2.117×10⁻¹⁰ m) because of neglect of configuration interaction. Therefore, to obtain a comparison with H₂-H₂ experiment, results from this report for large intermolecular distances were faired into ab initio results for small intermolecular distances. The resulting integrated absorption coefficient at 298 K for the pressure-induced fundamental vibrational transition was 87 percent of the experimental value.
INTRODUCTION

In certain high-temperature propulsion devices including gas-core nuclear rockets, an important mechanism of heat transfer is radiant energy exchange. In the gas-core rocket this radiation occurs between the uranium plasma and the hydrogen gas and between the hydrogen and the wall (refs. 1 and 2). Because of the high pressures in such devices, it is necessary to know the strength of pressure-induced infrared absorption of hydrogen to calculate the heat transfer (ref. 3). This strength is also necessary in constructing models of late-type stars (ref. 4). The strength depends on the interaction energies and the electric dipole moments occurring in the collisions of H₂ molecules with various collision partners. In the cases mentioned, important collision partners include H₂ and He and probably H. No experimental data taken much above room temperature exist for collision partners H₂ and He, and none at all for H. The present investigation is restricted to calculating the electric dipole moment and its derivative for collision partners H₂ and H, and is part of a project to calculate pressure-induced vibrational strengths for temperatures of 600 to 7000 K.

Pressure-induced absorption by an H₂ molecule occurs when a photon is absorbed because of the electric dipole moment resulting from the proximity of a collision partner. To conserve energy, the relative kinetic energy of the colliding molecules or the internal energy of H₂, or both, must change. If only the relative kinetic energy changes, the process is called pressure-induced translational absorption. If the H₂ rotational energy changes but not the vibrational energy, the process is termed pressure-induced rotational absorption. If the H₂ vibrational energy changes, the process is referred to as pressure-induced vibrational absorption. Vibrational absorption is the most important of these three processes in heat transfer at the temperatures in propulsion devices because it occurs at the shortest infrared wavelengths, which are nearest the peak of the Planck (blackbody) function.

For large intermolecular distances the electric dipole moment which occurs when H₂ collides with an atom or homonuclear diatomic molecule may be assumed to be the sum of two contributions. The quadrupole-induced contribution is due to the dipole moment induced in the atom or in the homonuclear diatomic molecule by the quadrupole moment of H₂. If the collision partner is a homonuclear diatomic molecule, its quadrupole moment may also induce a dipole moment in H₂. In this case, the two dipole moments are additive. The other contribution to the dipole moment comes from the distortion of the electron charge clouds of the two colliding molecules which results from their overlap. This contribution is much more difficult to calculate than the first and is the principal subject of this report. The overlap contribution is most important in pressure-induced vibrational absorption, which is the process emphasized herein. In vibrational absorption the derivative of the dipole moment with respect to H₂ inter-
nuclear distance is of much greater importance than the value of the dipole moment itself.

A number of theoretical investigations have been relevant to pressure-induced vibrational absorption by H2. Van Kranendonk and Bird (ref. 5) gave a semiempirical theory for the overlap contribution in H2-H2 collisions based on the distortion of the orbitals of two isolated repelling H atoms. They calculated what they called an "indirect" effect in the overlap contribution. When this was added to the quadrupole-induced contribution, their vibrational absorption coefficients were lower than measured. Britton and Crawford (ref. 6) added a "direct" effect to Van Kranendonk and Bird's results to get good agreement with absorption experiments at room temperature. Van Kranendonk (refs. 7 and 8) took quantum corrections to the pair distribution function into account to obtain an absorption coefficient theory applicable down to 150 K. None of these investigators considered configuration interaction because they were interested only in intermolecular distances of 4 bohr (2.117×10^-10 m) and greater. Kolos and Wolniewicz have since calculated more accurate values of H2 quadrupole moment and polarizability (refs. 9 and 10, respectively). Patch (ref. 11) has done an ab initio calculation of interaction energy and dipole moment and its derivative for H2-H2, which includes configuration interaction and therefore is believed to be valid for intermolecular distances of 4 bohr (2.117×10^-10 m) or less. These small distances become important well above room temperature. No investigations of pressure-induced H2-H absorption have been made.

This report calculates dipole moments and their derivatives for H2-H2 and H2-H for intermolecular distances of 4 bohr (2.117×10^-10 m) and greater. At such distances, accurate ab initio calculations are impractical on present day computers, so the semiempirical model of references 5 and 6 was used. It was refined for H2-H2 and had to be reformulated for H2-H.

The main body of the report is divided into two parts: one for H2-H2 and for H2-H. Each part is divided into an analysis section and a results and discussion section. The analysis section contains the derivation and points out the differences between it and references 5 and 6. The results and discussion section gives numerical results, comparisons with previous H2-H2 investigations, limitations, and potential applications.

**DIPOLE MOMENT AND ITS DERIVATIVE IN H2-H2 COLLISIONS**

**Analysis**

In the Born-Oppenheimer approximation and for intermolecular distances of 4 bohr (2.117×10^-10 m) or greater, the dipole moment of H2-H2 and its derivative consist of
two additive contributions: an overlap contribution and a quadrupole-induced contribution (refs. 5 and 6). In this section the overlap contribution is calculated from the semiempirical model of references 5 and 6 with the following refinements:

1. Previously neglected terms are included.
2. The repulsive distortion parameter $\lambda$ is based on a repulsive H-H calculation using the same orbital exponent as for $H_2$.
3. A nonplanar configuration is included.
4. The dipole moment, as well as its derivative, is obtained.

The overlap contribution is then expanded in spherical harmonics. Corrected equations for the expansion coefficients of the quadrupole-induced contribution to the derivative of the dipole moment (including anisotropy of $H_2$ polarizability) are given, together with expansion coefficients for the quadrupole-induced contribution to the dipole moment itself. All equations are in atomic units (bohr, hartree, and electron charge).

Coordinates. - The coordinate system is shown in figure 1. The origin of the Cartesian coordinates $x_1$, $x_2$, and $x_3$ is on the intermolecular axis halfway between molecules a-b and c-d (symbols are given in the appendix). The relative positions of the molecules are given by polar angles $\theta_1$ and $\theta_2$ and azimuthal angles $\varphi_1$ and $\varphi_2$. Only the $x_3$ component of the dipole moment and its derivative are considered for $H_2-H_2$ because Britton and Crawford (ref. 6) showed that the other components have only minor importance.

Overlap contribution to dipole moment. - For intermolecular distances of 4 bohr ($2.117 \times 10^{-10}$ m) or greater, it is reasonable to neglect configuration interaction, so the antisymmetric system wave function $\Psi$ was assumed to be
\[ \Psi = \psi_1 - \psi_3 - \psi_4 + \psi_5 \]  

where the determinantal wave functions \( \psi_1 \) and \( \psi_3 \) to \( \psi_5 \) are given by

\[
\begin{align*}
\psi_1 &= (4!)^{-1/2} \det \left[ a(1)\alpha(1), b(2)\beta(2), c(3)\alpha(3), d(4)\beta(4) \right] \\
\psi_3 &= (4!)^{-1/2} \det \left[ a(1)\alpha(1), b(2)\beta(2), c(3)\beta(3), d(4)\alpha(4) \right] \\
\psi_4 &= (4!)^{-1/2} \det \left[ a(1)\beta(1), b(2)\alpha(2), c(3)\alpha(3), d(4)\beta(4) \right] \\
\psi_5 &= (4!)^{-1/2} \det \left[ a(1)\beta(1), b(2)\alpha(2), c(3)\beta(3), d(4)\alpha(4) \right]
\end{align*}
\]  

Here \( a(1) \) is an atomic orbital for electron 1 centered on proton a and similarly for \( b(2) \), etc. Also, \( \alpha(1) \) is the spin eigenfunction of electron 1 with the component of spin angular momentum along the axis of quantization equal to \( \hbar /2 \), and \( \beta(3) \) is the spin eigenfunction of electron 3 with the component of spin angular momentum along the axis of quantization equal to \( -\hbar /2 \).

The \( x_3 \) component of the overlap dipole moment \( \mu_a \) is given by

\[
\mu_{ax_3} = \frac{\int \Psi^2 \left( \sum_p x_{3p} \sum_{i=1}^4 x_{3i} \right) dV_1 dV_2 dV_3 dV_4}{\int \Psi^2 dV_1 dV_2 dV_3 dV_4}
\]  

where \( x_{3p} \) is the \( x_3 \) coordinate of proton \( p \), and the \( p \) under the summation sign indicates summation over all protons. Similarly, \( x_{3i} \) is the \( x_3 \) coordinate of electron \( i \). The integration is over configuration and spin space of the four electrons. Equation (3) readily simplifies to

\[
\mu_{ax_3} = \frac{-\int \Psi^2 \sum_{i=1}^4 x_{3i} dV_1 dV_2 dV_3 dV_4}{\int \Psi^2 dV_1 dV_2 dV_3 dV_4}
\]  

\( \mu_{ax_3} \)
Equation (4) may be simplified by noting the properties of products of determinantal wave functions (ref. 12) and by introducing the following five types of integrals:

\[ S_{ab} = \int a(1)b(1)dv_1 \quad (a \text{ and } b \text{ in same molecule}) \]  
\[ S_{ac} = \int a(1)c(1)dv_1 \quad (a \text{ and } c \text{ in different molecules}) \]  
\[ m_{3aa} = \int a^2(1)x_{3a1}dv_1 \]  
\[ m_{3ab} = \int a(1)b(1)x_{3ab1}dv_1 \quad (a \text{ and } b \text{ in same molecule}) \]  
\[ m_{3ac} = \int a(1)c(1)x_{3ac1}dv_1 \quad (a \text{ and } c \text{ in different molecules}) \]

where \( x_{3a1} \) is the \( x_3 \) component of a vector from proton \( a \) to electron \( 1 \), \( x_{3ac1} \) is the \( x_3 \) component of a vector from the center of line \( ac \) to electron \( 1 \), and \( dv_1 \) is an element of volume for electron \( 1 \). In addition, it was assumed that

\[ \int a^2(1)dv_1 = 1 \]  

and likewise for similar integrals. Hence, equation (4) becomes

\[ \rho \cdot x_3 = \frac{N_1 + N_2 + N_3}{E} \]  

where

\[ N_1 = -4 \left[ (m_{3aa} + m_{3bb} + 2m_{3ab}S_{ab})(1 + S_{cd}^2) + (m_{3cc} + m_{3dd} + 2m_{3cd}S_{cd})(1 + S_{ab}^2) \right] \]
\[
N_2 = 4 \left[ m_{3ac}(s_{ac} + s_{ab} s_{bc} + S_{cd} s_{ad} + s_{ab} S_{cd} s_{bd}) + m_{3ad}(s_{ad} + s_{ab} s_{bd} + S_{cd} s_{ac})
\right. \\
\left. + s_{ab} S_{cd} s_{bd}) + m_{3bc}(s_{bc} + s_{ab} s_{ac} + S_{cd} s_{bd} + s_{ab} S_{cd} s_{ad})
\right. \\
+ m_{3bd}(s_{bd} + s_{ab} s_{ad} + S_{cd} s_{bc} + s_{ab} S_{cd} s_{ac}) \right]
\] (13)

\[
N_3 = 2 \left[ m_{3aa}(s_{bd}^2 + s_{bc}^2 + 2 S_{cd} s_{bc} s_{bd}) + m_{3bb}(s_{ad}^2 + s_{ac}^2 + 2 S_{cd} s_{ac} s_{ad}) + m_{3cc}(s_{bd}^2 + s_{ad}^2
\right. \\
\left. + 2 S_{ab} s_{ad} s_{bd}) + m_{3dd}(s_{bc}^2 + s_{ac}^2 + 2 S_{ab} s_{ac} s_{bc}) \right] + 4 \left\{ m_{3ab}[s_{ad} s_{bd}
\right. \\
+ s_{ac} s_{bc} + S_{cd}(s_{ac} s_{bd} + s_{ad} s_{bc}) \right. \left. + m_{3cd}[s_{bc} s_{bd} + s_{ac} s_{ad} \right. \\
\right. \\
+ s_{ab} (s_{ac} s_{bd} + s_{bc} s_{ad}) \right\} \right) 
\] (14)

\[
E = 4 (S_{cd}^2 + 1)(1 + S_{ab}) - 4 \left[ S_{ab}(s_{ad} s_{bd} + s_{ac} s_{bc}) + S_{cd}(s_{bc} s_{bd} + s_{ac} s_{ad}) \right] - 2(s_{bd}^2 + s_{ac}^2
\right. \\
\left. + s_{bc}^2 + s_{ad}^2) - 4 S_{ab} S_{cd}(s_{bc} s_{ad} + s_{ac} s_{bd}) \right) 
\] (15)

In equations (14) and (15), terms of order \(s^3\) and \(s^4\) were neglected because they were found to have negligible effect on \(\mu_{ax_3}\) or its derivative with respect to internuclear distance for any configuration or intermolecular distance in this report.

Following references 5 and 6, Rosen-like (ref. 13) orbitals were used, of the form

\[
a(1) = \left( \frac{\zeta^{3}_{ab}}{\pi} \right)^{1/2} e^{-\zeta_{ab} r_{a1}} (1 + \kappa_{ab} r_{a1} \cos \theta_{ab1} + \lambda_{ac} r_{a1} \cos \theta_{ac1} + \lambda_{ad} r_{a1} \cos \theta_{ad1}) 
\] (16)

where \(\theta_{ab1}\) is the angle at proton a between proton b and electron 1, etc., \(r_{a1}\) is the distance from proton a to electron 1, \(\kappa_{ab}\) is an attractive distortion parameter (always positive) for an isolated \(H_2\) molecule a-b, and \(\lambda_{ac}\) is a repulsive distortion parameter (always negative) for the two repelling atoms a and c. The terms in equation (16) containing \(\kappa_{ab}, \lambda_{ac},\) and \(\lambda_{ad}\) each have absolute values much less than 1, so \(a(1)\) is a
slightly distorted 1s atomic orbital. If $a^2(1)$ terms containing $\kappa^2$, $\kappa \lambda$, and $\lambda^2$ are neglected, equation (10) is satisfied. The orbital exponent $\xi_{ab}$ was assumed to have the same value as for an isolated H$_2$ molecule a-b (ref. 5 or 13) with internuclear distance $r_{ab}$.

The distortion parameters $\kappa_{ab}$, $\lambda_{ac}$, and $\lambda_{ad}$ were assumed to depend only on the distances $r_{ab}$, $r_{ac}$, and $r_{ad}$, respectively. The attractive distortion parameter for an isolated H$_2$ molecule can be found from reference 5 or 13. The repulsive distortion parameter $\lambda_{ac}$ was calculated by a variational method for two repelling H atoms a and c by assuming orbitals of the form

$$a(1) = \left(\frac{\xi}{\pi}\right)^{1/2} e^{-\xi r_{a1}} (1 + \lambda_{ac} r_{a1} \cos \theta_{ac1})$$  \hspace{1cm} (17)

The required variational method and integrals were given by Rosen (ref. 13) for molecular H$_2$, so for two repelling H atoms it was necessary to change the signs of all Rosen's exchange terms and correct typographical errors. In Rosen's method both $\xi$ and $\lambda_{ac}$ were optimized. In our version this would cause $\xi \neq \xi_{ab}$. To avoid this in calculating $\lambda_{ac}$ for use with H$_2$-H$_2$, $\xi$ was not optimized but was fixed at the value for the isolated H$_2$ molecule.

Integrals of the type $S_{ab}$ and $s_{ac}$ are known as overlap integrals. Because eventually equations (11) to (15) had to be differentiated with respect to $r_{ab}$ while holding $r_{cd}$ constant, the case $\xi_{ab} \neq \xi_{cd}$ had to be considered for $s_{ac}$ but did not affect $S_{ab}$. Hence, types $S_{ab}$ and $s_{ac}$ are treated separately below. However, in both types, terms containing $\kappa \lambda$, $\kappa^2$, $\lambda^2$, and $\lambda$ were neglected compared to terms containing $\kappa$.

Using spheroidal coordinates (ref. 14), integrals of type $S_{ab}$ were evaluated.

$$S_{ab} = (1 + \kappa_{ab} r_{ab}) e^{-\sigma_{ab}} \left(1 + \sigma_{ab} + \frac{\sigma_{ab}^2}{3}\right)$$ \hspace{1cm} (18)

where

$$\sigma_{ab} = \xi_{ab} r_{ab}$$ \hspace{1cm} (19)

Prolate spheroidal coordinates were also used for integrals of type $s_{ac}$, but the law of cosines from spherical trigonometry was also required. Let

$$\sigma_{ac} = \frac{1}{2} r_{ac} (\xi_{ab} + \xi_{cd})$$ \hspace{1cm} (20)
\[ \tau_{ac} = \frac{1}{2} r_{ac} (\xi_{ab} - \xi_{cd}) \] (21)

Then

\[ s_{ac} = \frac{1}{2} (\xi_{ab} + \xi_{cd})^{3/2} r_{ac}^3 e^{-\sigma_{ac}} \left( 2M(\sigma_{ac}) + r_{ac} \left\{ \kappa_{ab} \cos \theta_{abc} [M(\sigma_{ac}) - L(\sigma_{ac}, \tau_{ac})] + \kappa_{cd} \cos \theta_{cda} [M(\sigma_{ac}) + L(\sigma_{ac}, \tau_{ac})] \right\} \right) \] (22)

where

\[ M(\sigma) = \frac{1}{\sigma^3} + \frac{1}{\sigma^2} + \frac{1}{3\sigma} \] (23)

\[ L(\sigma, \tau) = \left( \frac{1}{\sigma^4} + \frac{1}{\sigma^3} + \frac{2}{5\sigma^2} + \frac{1}{15\sigma} \right) \tau \] (24)

and where, after integration, exponentials with arguments \( \pm \tau_{ac} \) were expanded in power series, and then terms of order \( \tau^2_{ac} \) and higher were neglected. Equations (1) to (24) are equivalent to those in reference 6.

For the integral \( m_{3aa} \) (eq. (7)), polar coordinates with origin at proton a and polar axis parallel to the \( x_3 \) axis were used. Terms containing \( \kappa^2 \), \( \kappa \lambda \), and \( \lambda^2 \) were neglected. It was necessary to use the law of cosines from spherical trigonometry to get

\[ m_{3aa} = \frac{2}{\xi_{ab}^2} \left( \kappa_{ab} \cos \theta_{abx_3} + \lambda_{ac} \cos \theta_{acx_3} + \lambda_{ad} \cos \theta_{adx_3} \right) \] (25)

where \( \theta_{abx_3} \) is the angle at proton a between proton b and a line through proton a parallel to the \( x_3 \) axis. Equations for \( m_{3bb} \), \( m_{3cc} \), and \( m_{3dd} \) were deduced from equation (25).

For integrals of the type \( m_{3ab} \) (eq. (8)), prolate spheroidal coordinates and the law of cosines from spherical trigonometry were necessary. Terms involving \( \kappa^2 \), \( \kappa \lambda \), and \( \lambda^2 \) were neglected. The relation

\[ x_{3ab1} = \frac{x_{3a1} + x_{3b1}}{2} \] (26)
was needed. The result was

\[
\begin{align*}
m_{3ab} &= -\frac{1}{4} \zeta^3 ab r_{ab}^5 e^{-\sigma_{ab}} \left\{ \lambda_{ac} \cos \theta_{abc} \cos \theta_{abx} \right. \\
&\quad \left. + \sin \theta_{abc} \sin \theta_{abx} \cos \varphi_{cabx} T(\sigma_{ab}) \right. \\
&\quad \left. + \cos \theta_{abd} \cos \theta_{abx} \cos \varphi_{dabx} U(\sigma_{ab}) \right. \\
&\quad \left. + \sin \theta_{bdc} \sin \theta_{abx} \cos \varphi_{cabx} T(\sigma_{ab}) \right. \\
&\quad \left. + \lambda_{bd} \cos \theta_{bad} \cos \theta_{abx} \right. \\
&\quad \left. \cos \varphi_{dabx} U(\sigma_{ab}) \right. \\
&\quad \left. + \sin \theta_{bad} \sin \theta_{abx} \cos \varphi_{dabx} T(\sigma_{ab}) \right. \right\}
\end{align*}
\]

(27)

where \( \varphi_{cabx} \) is the dihedral angle between plane \( cab \) and a plane containing the line \( ab \) and the \( x_3 \) axis and where

\[
T(\sigma) = \frac{4}{\sigma^5} + \frac{4}{\sigma^4} + \frac{8}{5\sigma^3} + \frac{4}{15\sigma^2}
\]

(28)

\[
U(\sigma) = \frac{4}{\sigma^5} + \frac{4}{\sigma^4} + \frac{9}{5\sigma^3} + \frac{7}{15\sigma^2} + \frac{1}{15\sigma}
\]

(29)

Integrals of the type \( m_{3ac} \) (eq. (9)) were treated like type \( m_{3ab} \), except for the
orbital exponents, which may be unequal. The result was

\[
m_{3ac} = \frac{1}{4} \left( \frac{r_{ab} r_{cd}}{c_{ac} c_{cd}} \right)^{3/2} \exp \left( -2 \cos \theta_{acx} \right) L(\sigma_{ac}, \tau_{ac}) \left( \frac{1}{r_{ac}} + \lambda_{ac} \right) + \kappa_{ab} \left\{ \cos \theta_{abc} \cos \theta_{acx} \left[ U(\sigma_{ac}) - L(\sigma_{ac}, \tau_{ac}) \right] + \sin \theta_{abc} \sin \theta_{acx} \cos \varphi_{bacx} T(\sigma_{ac}) \right\} + \kappa_{cd} \left\{ \cos \theta_{cad} \cos \theta_{acx} \left[ -U(\sigma_{ac}) - L(\sigma_{ac}, \tau_{ac}) \right] + \sin \theta_{cad} \sin \theta_{acx} \cos \varphi_{dacx} T(\sigma_{ac}) \right\} + \lambda_{ad} \left\{ \cos \theta_{acd} \cos \theta_{acx} \left[ U(\sigma_{ac}) - L(\sigma_{ac}, \tau_{ac}) \right] + \sin \theta_{acd} \sin \theta_{acx} \cos \varphi_{dax} T(\sigma_{ac}) \right\} + \lambda_{bc} \left\{ \cos \theta_{cab} \cos \theta_{acx} \left[ -U(\sigma_{ac}) - L(\sigma_{ac}, \tau_{ac}) \right] + \sin \theta_{cab} \sin \theta_{acx} \cos \varphi_{bacx} T(\sigma_{ac}) \right\} \right) \tag{30}
\]

where, after integration, exponentials with arguments \( \pm \tau_{ac} \) were expanded in power series and then terms of order \( \tau_{ac}^2 \) and higher were neglected. The angle \( \varphi_{bacx} \) is the dihedral angle between plane bac and a plane containing line ac and parallel to the \( x_3 \) axis.

Overlap contribution to derivative of dipole moment. - In calculating the pressure-induced vibrational absorption, the partial derivative of the \( x_3 \) component of the dipole moment with respect to the internuclear distance \( r_{ab} \) is the most important variable. If we let a prime indicate \( \partial / \partial r_{ab} \) from equation (11)

\[
\mu'_{ax} = \frac{N'_1 + N'_2 + N'_3}{E} - \frac{(N_1 + N_2 + N_3)E'}{E^2} \tag{31}
\]

The terms \( N'_1, N'_2, N'_3, \) and \( E' \) were found by differentiating equations (12) to (15), but the results are too lengthy to reproduce here. To find \( N'_1, N'_2, N'_3, \) and \( E' \), the derivatives of the molecular integrals were required. These were found analytically from equations (18) to (25) and (27) to (30) and are also too lengthy to reproduce here.
general, in taking the derivative with respect to $r_{ab}$ it should be noted that $\zeta_{ab}$, $k_{ab}$, $r_{ac}$, $r_{ad}$, $r_{bc}$, $r_{bd}$, $\lambda_{ac}$, $\lambda_{ad}$, $\lambda_{bd}$ and most of the $\theta$'s and $\varphi$'s with letter subscripts are functions of $r_{ab}$.

A comparison of the assumptions made in references 5 and 6 and in this report in calculating $\mu'_{ax_3}$ is presented in table I.

### TABLE I. - COMPARISON OF ASSUMPTIONS MADE AND CONFIGURATIONS USED BY VARIOUS INVESTIGATORS IN CALCULATING OVERLAP CONTRIBUTION TO DERIVATIVE OF DIPOLE MOMENT IN $H_2 - H_2$ COLLISIONS

<table>
<thead>
<tr>
<th>Antisymmetric system wave function, $\psi$</th>
<th>Van Kranendonk and Bird (ref. 5)</th>
<th>Britton and Crawford (ref. 6)</th>
<th>This report</th>
</tr>
</thead>
<tbody>
<tr>
<td>Only $x_3$ component of $\mu'_a$</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Type $m_{3ac}$ integrals, as well as type $m_{3ac}$, retained in $N_2^2$</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>$N_3$ included in $\mu'_{ax_3}$</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Terms of order $s^2$ retained in final expression for $E$</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>$(N_1 + N_2 + N_3)E'/E^2$ retained in $\mu'_{ax_3}$</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Value of orbital exponent $\zeta$ in calculation of $\lambda$, bohr$^{-1}$ (m$^{-1}$)</td>
<td>1.000 (1.890$\times$10$^{10}$)</td>
<td>1.000 (1.890$\times$10$^{10}$)</td>
<td>1.174 (2.219$\times$10$^{10}$)</td>
</tr>
<tr>
<td>Factor of $1 + \kappa r$ in integrals of type $S_{ab}$</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Complete expression for integrals of type $m_{3ac}$ and $m_{3ac}'$, except for neglect of terms of order $r_{ac}^2$ and higher</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>$r_{ac}'$, $r_{ad}'$, $r_{bc}'$, and $r_{bd}'$ included in derivatives of integrals</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>$\lambda'$ included in derivatives of integrals</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>$\theta'$ and $\varphi'$ (with letter subscripts) included in derivatives of integrals</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Number of planar configurations included</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Number of nonplanar configurations included</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Equilibrium internuclear distance of $H_2$ molecules, bohr(m)</td>
<td>a$1.416$ (0.7493$\times$10$^{-10}$)</td>
<td>a$1.416$ (0.7493$\times$10$^{-10}$)</td>
<td>b$1.401446$ (0.741599$\times$10$^{-10}$)</td>
</tr>
<tr>
<td>$D_{2-222}$ and $D_{222-2}$ included in $\mu'_{ax_3}$ expansion</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

*a* Equilibrium internuclear distance for Rosen model (ref. 13).

*b* Equilibrium internuclear distance from spectroscopic data (ref. 16).
Configurations and expansion coefficients. - In calculating the pressure-induced vibrational absorption, $\mu_{x3}^1$ is always expanded in spherical harmonics $Y_{l\mu}$ (refs. 5 and 6).

$$\mu_{x3}^1 = \sum_{l_1=0}^{\infty} \sum_{\mu_1=-l_1}^{l_1} \sum_{l_2=0}^{\infty} \sum_{\mu_2=-l_2}^{l_2} 2\pi D_{l_1\mu_1}D_{l_2\mu_2}^0 (R) Y_{l_1\mu_1}^1(\theta_1, \varphi_1)Y_{l_2\mu_2}^1(\theta_2, \varphi_2)$$

(32)

where

$$Y_{l\mu}(\theta, \varphi) = (2\pi)^{-1/2} \Theta_{l\mu}(\theta) e^{i\mu \varphi}$$

(33)

and $\Theta_{l\mu}(\theta)$ are normalized associated Legendre functions tabulated by Pauling and Wilson (ref. 12) for $\mu \geq 0$. For $\mu < 0$, we take $\Theta_{l\mu} = (-1)^\mu \Theta_{l\mu}$. The fact that molecules a-b and c-d were homonuclear required that many of the D's be 0 because of symmetry. In addition, we restricted our calculations to the five configurations shown in figure 2. Thus, the only nonzero D's that could be determined were $D_{0000}$, $D_{2000}$.

![Figure 2. Configurations used in calculations for H_2-H_2 collisions. Intermolecular distance R had values from 4 to 8 bohr (2.117 x 10^{-10} ml) to 4.233 x 10^{-10} ml, which is the equilibrium value (ref. 16).](image-url)
TABLE II - POLAR AND AZIMUTHAL ANGLES FOR FIVE CONFIGURATIONS SHOWN IN FIGURE 2

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Polar angle of molecule a-b, ( \theta_1 ), deg</th>
<th>Polar angle of molecule c-d, ( \theta_2 ), deg</th>
<th>Azimuthal angle of molecule a-b, ( \phi_1 ), deg</th>
<th>Azimuthal angle of molecule c-d, ( \phi_2 ), deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>90</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>90</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>90</td>
<td>90</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
</tbody>
</table>

\[ D_{0020}, D_{2020}, D_{2-222} \text{ and } D_{222-2} \text{ (the last two are equal).} \]

Let \( \left( \mu_{x3}^r \right)_i \) be \( \mu_{x3}^r \) for the \( i^{th} \) configuration. Then from equations (32) and (33) and table II,

\[
\begin{align*}
\left( \mu_{x3}^r \right)_1 &= \frac{1}{2} D_{0000} + \sqrt{\frac{5}{4}} D_{2000} + \sqrt{\frac{5}{4}} D_{0020} + \frac{5}{2} D_{2020} \\
\left( \mu_{x3}^r \right)_2 &= \frac{1}{2} D_{0000} - \sqrt{\frac{5}{16}} D_{2000} - \sqrt{\frac{5}{16}} D_{0020} + \frac{5}{8} D_{2020} + \frac{15}{8} D_{2-222} \\
\left( \mu_{x3}^r \right)_3 &= \frac{1}{2} D_{0000} + \sqrt{\frac{5}{16}} D_{2000} - \sqrt{\frac{5}{16}} D_{0020} - \frac{5}{4} D_{2020} \\
\left( \mu_{x3}^r \right)_4 &= \frac{1}{2} D_{0000} - \sqrt{\frac{5}{16}} D_{2000} + \sqrt{\frac{5}{4}} D_{0020} - \frac{5}{4} D_{2020} \\
\left( \mu_{x3}^r \right)_5 &= \frac{1}{2} D_{0000} - \sqrt{\frac{5}{16}} D_{2000} - \sqrt{\frac{5}{16}} D_{0020} + \frac{5}{8} D_{2020} - \frac{15}{8} D_{2-222}
\end{align*}
\]

where the equality of \( D_{2-222} \) and \( D_{222-2} \) was invoked. Equations (34) were solved for \( D \).
In calculating pressure-induced translational or rotational absorption with any model, or pressure-induced vibrational absorption with anharmonicity and H₂ vibration-rotation interaction, \( \mu_{x_3} \) is also expanded in spherical harmonics

\[
D_{0000} = \frac{2}{9} \left( \mu_{x_3} \right)_1 + \frac{4}{9} \left( \mu_{x_3}^* \right)_2 + \frac{4}{9} \left( \mu_{x_3}^* \right)_3 + \frac{4}{9} \left( \mu_{x_3}^* \right)_4 + \frac{4}{9} \left( \mu_{x_3}^* \right)_5 \\
D_{2000} = \frac{4}{9 \sqrt{5}} \left( \mu_{x_3}^* \right)_1 - \frac{4}{9 \sqrt{5}} \left( \mu_{x_3}^* \right)_2 + \frac{8}{9 \sqrt{5}} \left( \mu_{x_3}^* \right)_3 - \frac{4}{9 \sqrt{5}} \left( \mu_{x_3}^* \right)_4 - \frac{4}{9 \sqrt{5}} \left( \mu_{x_3}^* \right)_5 \\
D_{0020} = \frac{4}{9 \sqrt{5}} \left( \mu_{x_3}^* \right)_1 - \frac{4}{9 \sqrt{5}} \left( \mu_{x_3}^* \right)_2 - \frac{4}{9 \sqrt{5}} \left( \mu_{x_3}^* \right)_3 + \frac{8}{9 \sqrt{5}} \left( \mu_{x_3}^* \right)_4 - \frac{4}{9 \sqrt{5}} \left( \mu_{x_3}^* \right)_5 \\
D_{2020} = \frac{8}{45} \left( \mu_{x_3}^* \right)_1 + \frac{4}{45} \left( \mu_{x_3}^* \right)_2 - \frac{8}{45} \left( \mu_{x_3}^* \right)_3 - \frac{8}{45} \left( \mu_{x_3}^* \right)_4 + \frac{4}{45} \left( \mu_{x_3}^* \right)_5 \\
D_{2-222} = \frac{4}{15} \left( \mu_{x_3}^* \right)_2 - \frac{4}{15} \left( \mu_{x_3}^* \right)_5 \\
\] (35)

In calculating pressure-induced translational or rotational absorption with any model, or pressure-induced vibrational absorption with anharmonicity and H₂ vibration-rotation interaction, \( \mu_{x_3} \) is also expanded in spherical harmonics

\[
\mu_{x_3} = \sum_{l_1=0}^{\infty} \sum_{\mu_1=-l_1}^{l_1} \sum_{l_2=0}^{\infty} \sum_{\mu_2=-l_2}^{l_2} 2\pi c_{l_1 l_2} \mu_1 \mu_2 \mu_3 (R) Y_{l_1 \mu_1} (\theta_1, \phi_1) Y_{l_2 \mu_2} (\theta_2, \phi_2) \quad (36)
\]

Due to the symmetry required by homonuclear diatomic molecules and due to the limitation to the five configurations in figure 2, the only C's that might be nonzero that can be determined are \( C_{0000}, C_{2000}, C_{0020}, C_{2020}, C_{2-222}, \) and \( C_{222-2} \) (the last two are equal). By symmetry, \( \mu_{x_3} \) is zero for configurations 1, 2, and 5 and

\[
\left( \mu_{x_3} \right)_3 = - \left( \mu_{x_3} \right)_4 \\
\] (37)

Combining equations (33), (36), and (37), using table II, and invoking the equality of \( C_{2-222} \) and \( C_{222-2} \) gave
\[ 0 = \frac{1}{2} C_{0000} + \sqrt{\frac{5}{4}} C_{2000} + \sqrt{\frac{5}{4}} C_{0020} + \frac{5}{2} C_{2020} \]

\[ 0 = \frac{1}{2} C_{0000} - \sqrt{\frac{5}{16}} C_{2000} - \sqrt{\frac{5}{16}} C_{0020} + \frac{5}{8} C_{2020} + \frac{15}{8} C_{2-222} \]

\[ \left( \mu_{x_3} \right)_3 = \frac{1}{2} C_{0000} + \sqrt{\frac{5}{4}} C_{2000} - \sqrt{\frac{5}{16}} C_{0020} - \frac{5}{4} C_{2020} \]

\[ - \left( \mu_{x_3} \right)_3 = \frac{1}{2} C_{0000} - \sqrt{\frac{5}{16}} C_{2000} + \sqrt{\frac{5}{4}} C_{0020} - \frac{5}{4} C_{2020} \]

\[ 0 = \frac{1}{2} C_{0000} - \sqrt{\frac{5}{16}} C_{2000} - \sqrt{\frac{5}{16}} C_{0020} + \frac{5}{8} C_{2020} - \frac{15}{8} C_{2-222} \]

analogous to equation (34). The solution of equations (38) is \( C_{0000} = C_{2020} = C_{2-222} = 0 \) and

\[ C_{2000} = \frac{4}{3 \sqrt{5}} \left( \mu_{x_3} \right)_3 = - C_{0020} \]

(39)

Although equations (32) to (39) were derived for \( \mu_{x_3} \) and \( \mu_{x_3} \), they are linear and therefore each is applicable to the overlap and quadrupole-induced contributions separately, where

\[ \mu_{x_3} = \mu_{ax_3} + \mu_{qx_3} \]

(40)

\[ \mu_{x_3}' = \mu_{ax_3}' + \mu_{qx_3}' \]

(41)

\[ C_{l_1 l_2 l_2 l_2} = C_{al_1 l_1 l_2} + C_{ql_1 l_1 l_2} \]

(42)

\[ D_{l_1 l_1 l_2 l_2} = D_{al_1 l_1 l_2} + D_{ql_1 l_1 l_2} \]

(43)

with subscript a standing for overlap contribution and subscript q for quadrupole-induced contribution.
**Quadrupole-induced contribution to dipole moment.** - An H atom does not have a quadrupole moment. However, an H₂ molecule has a permanent quadrupole moment because of the correlation of the electrons. This correlation was neglected in estimating the distortion of the orbitals in the overlap calculations. Therefore these calculations include neither the dipole moment induced in molecule c-d by the quadrupole moment of molecule a-b nor the dipole moment induced in molecule a-b by the quadrupole moment of molecule c-d. These quadrupole-induced contributions must thus be added to the overlap contributions to $\mu_{x_3}$ (eq. (40)). The expansion coefficients for these quadrupole-induced contributions were given by Colpa and Ketelaar (ref. 15), and for the $x_3$ component are (after correcting a typographical error and allowing for the difference in definition of $\Theta_{l\mu}$)

\[
\begin{align*}
C_{q0000} &= 0 \\
C_{q2000} &= \frac{6\sqrt{5}}{5} \frac{Q_{ab} \alpha_{cd}}{R^4} \\
C_{q0020} &= -\frac{6\sqrt{5}}{5} \frac{Q_{cd} \alpha_{ab}}{R^4} \\
C_{q2020} &= \frac{4}{5R^4} (Q_{ab} \Delta_{cd} - Q_{cd} \Delta_{ab}) \\
C_{q212-1} &= \frac{2}{5R^4} (Q_{ab} \Delta_{cd} - Q_{cd} \Delta_{ab}) \\
C_{q222-1} &= 0 \\
C_{q222-2} &= 0
\end{align*}
\]

where $Q_{ab}$ is the scalar quadrupole moment of molecule a-b defined by

\[
Q_{ab} = -Q_{XX} = -Q_{YY} = \frac{1}{2} Q_{ZZ}
\]

Here X, Y, and Z are Cartesian coordinates with origin at the midpoint of the line connecting a and b, with Z running along line ab. The quantities $Q_{XX}$, $Q_{YY}$, and $Q_{ZZ}$ are elements of the quadrupole moment tensor of molecule a-b. The quantities $\alpha_{ab}$ and $\Delta_{ab}$ are the average polarizability and anisotropy of the polarizability, respectively, of molecule a-b. Equations (44) may all be written
\[ C_{ll_1l_2\mu_1\mu_2} = \frac{c_{ll_1l_2\mu_1\mu_2}}{R^4} \]  

(46)

where each \( c_{ll_1l_2\mu_1\mu_2} \) is a constant.

**Quadrupole-induced contribution to derivative of dipole moment.** - The expansion coefficients for the quadrupole-induced contribution to the \( x_3 \) component of the dipole moment were found by differentiating equations (44) with respect to \( r_{ab} \). For \( r_{ab} = r_{cd} \) they are

\[
\begin{align*}
D_{q0000} &= 0 \\
D_{q2000} &= \frac{6\sqrt{5}}{5} \frac{Q'\alpha}{R^4} \\
D_{q0020} &= -\frac{6\sqrt{5}}{5} \frac{Q\alpha'}{R^4} \\
D_{q2020} &= \frac{4}{5} \frac{Q'\Delta - Q\Delta'}{R^4}
\end{align*}
\]

\[
\begin{align*}
D_{q2-121} &= \frac{2}{5} \frac{Q'\Delta - Q\Delta'}{R^4} \\
D_{q212-1} &= \frac{2}{5} \frac{Q'\Delta - Q\Delta'}{R^4} \\
D_{q2-222} &= 0 \\
D_{q222-2} &= 0
\end{align*}
\]

(47)

The nonzero expressions for \( D_{q0000} \) in reference 6 are incorrect. Equations (47) may all be written

\[ D_{ql_1l_2\mu_1\mu_2} = \frac{d_{ql_1l_2\mu_1\mu_2}}{R^4} \]

(48)

where each \( d_{ql_1l_2\mu_1\mu_2} \) is a constant.

**Results and Discussion**

**Repulsive distortion parameter.** - This parameter was calculated with a digital computer as discussed in the section Analysis. The orbital exponent was fixed at
1.174 bohr\(^{-1}\) (2.219×10\(^{10}\) m\(^{-1}\)), which is the value for an H\(_2\) molecule with internuclear distance of 1.401446 bohr (0.741599×10\(^{-10}\) m) according to Rosen's model (ref. 5). This internuclear distance is the H\(_2\) equilibrium internuclear distance obtained from spectroscopic data (ref. 16) and was used for consistency with the integrated absorption coefficient calculations (see comparison with experiment). The results for the repulsive distortion parameter are given in table III.

**TABLE III. - REPULSIVE DISTORTION PARAMETER FOR TWO REPELLING H ATOMS**

<table>
<thead>
<tr>
<th>Internuclear distance, (r)</th>
<th>Orbital exponent of both atoms, (\zeta)</th>
<th>Used in H(_2)-H calculations</th>
<th>Used in H(_2)-H(_2) calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>bohr(^{-1})</td>
<td>m (\times 10^{-10})</td>
<td>bohr(^{-1})</td>
<td>m (\times 10^{-10})</td>
</tr>
<tr>
<td>2.5</td>
<td>0.1323×10(^{-9})</td>
<td>-0.8179×10(^{-1})</td>
<td>-0.1546×10(^{10})</td>
</tr>
<tr>
<td>3.0</td>
<td>0.1588</td>
<td>-0.4760</td>
<td>-0.8995×10(^{9})</td>
</tr>
<tr>
<td>3.5</td>
<td>0.1852</td>
<td>-0.2716</td>
<td>-0.5133</td>
</tr>
<tr>
<td>4.0</td>
<td>0.2117</td>
<td>-0.1509</td>
<td>-0.2852</td>
</tr>
<tr>
<td>4.5</td>
<td>0.2381</td>
<td>-0.8114×10(^{-2})</td>
<td>-0.1533</td>
</tr>
<tr>
<td>5.0</td>
<td>0.2646</td>
<td>-0.4217</td>
<td>-0.7969×10(^{8})</td>
</tr>
<tr>
<td>5.5</td>
<td>0.2910</td>
<td>-0.2120</td>
<td>-0.4006</td>
</tr>
<tr>
<td>6.0</td>
<td>0.3175</td>
<td>-0.1034</td>
<td>-0.1954</td>
</tr>
<tr>
<td>6.5</td>
<td>0.3440</td>
<td>-0.4905×10(^{-3})</td>
<td>-0.9269×10(^{7})</td>
</tr>
<tr>
<td>7.0</td>
<td>0.3704</td>
<td>-0.2273</td>
<td>-0.4295</td>
</tr>
<tr>
<td>7.5</td>
<td>0.3969</td>
<td>-0.1032</td>
<td>-0.1950</td>
</tr>
<tr>
<td>8.0</td>
<td>0.4233</td>
<td>-0.4602×10(^{-4})</td>
<td>-0.8697×10(^{6})</td>
</tr>
<tr>
<td>8.5</td>
<td>0.4498</td>
<td>-0.2029</td>
<td>-0.3817</td>
</tr>
<tr>
<td>9.0</td>
<td>0.4763</td>
<td>-0.8747×10(^{-5})</td>
<td>-0.1653</td>
</tr>
<tr>
<td>9.5</td>
<td>0.5027</td>
<td>-0.3744</td>
<td>-0.7075×10(^{5})</td>
</tr>
</tbody>
</table>

Overlap contributions to \(\mu_x^3\) and \(\mu_x^l\). - These contributions were calculated from equations (11) to (15), (18) to (25), and (27) to (31) by using a digital computer. The H\(_2\) internuclear distance had the value of 1.401446 bohr (0.741599×10\(^{-10}\) m) for the reasons previously given. The values of \(\kappa\) and \(\zeta\) were calculated from reference 5 for this internuclear distance and were 0.1205 bohr\(^{-1}\) (0.2277×10\(^{10}\) m\(^{-1}\)) and 1.174 bohr\(^{-1}\) (2.219×10\(^{10}\) m\(^{-1}\)), respectively. The values of \(\kappa'\) and \(\zeta'\) were assumed to be the same as for the internuclear distance of 1.416 bohr (0.7493×10\(^{-10}\) m) and were
### TABLE IV. - EXPANSION COEFFICIENTS FOR $x_3$ COMPONENT OF OVERLAP DIPOLE MOMENT AND ITS DERIVATIVE IN H$_2$-H$_2$ COLLISIONS

<table>
<thead>
<tr>
<th>Intermolecular distance, $\rho$</th>
<th>Expansion coefficient for overlap dipole moment, $a_{\rho 000}$</th>
<th>Expansion coefficients for derivative of overlap dipole moment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_{\rho 0000}$</td>
<td>$D_{\rho 2000}$</td>
</tr>
<tr>
<td>$m$</td>
<td>$n$</td>
<td>$a$</td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
<td>----</td>
</tr>
<tr>
<td>6.0</td>
<td>0.2117x10^3</td>
<td>-0.5042x10^-3</td>
</tr>
<tr>
<td>4.3</td>
<td>0.2223</td>
<td>-0.4701</td>
</tr>
<tr>
<td>4.4</td>
<td>0.2328</td>
<td>-0.3768</td>
</tr>
<tr>
<td>4.6</td>
<td>0.2434</td>
<td>-0.2928</td>
</tr>
<tr>
<td>4.8</td>
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<td>-0.2255</td>
</tr>
<tr>
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<td>0.2646</td>
<td>-0.1729</td>
</tr>
<tr>
<td>5.2</td>
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</tr>
<tr>
<td>5.4</td>
<td>0.2858</td>
<td>-0.1013</td>
</tr>
<tr>
<td>5.6</td>
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<td>-0.7738x10^-4</td>
</tr>
<tr>
<td>5.8</td>
<td>0.3069</td>
<td>-0.5900</td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
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</tr>
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<td>7.4</td>
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<td>-0.5013</td>
</tr>
<tr>
<td>7.6</td>
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<tr>
<td>7.8</td>
<td>0.4128</td>
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</tr>
<tr>
<td>8.0</td>
<td>0.4233</td>
<td>-0.2347</td>
</tr>
</tbody>
</table>

$a_{Ca0020} = \frac{a_{Ca0020}}{D_{Ca0020}}$
-0.037 bohr\(^{-2}\) (-0.132\times10^{20}\) m\(^{-2}\)) and -0.247 bohr\(^{-2}\) (-0.882\times10^{20}\) m\(^{-2}\)), respectively (ref. 5). The calculations were carried out for the five configurations in figure 2 and for intermolecular distances from 4 to 8 bohr (2.117\times10^{-10} to 4.233\times10^{-10}\) m). The expansion coefficients are tabulated in table IV.

Quadrupole-induced contributions to $\mu_{x_3}^q$ and $\mu_{x_3}'$. - These contributions required values for $Q$, $\alpha$, and $\Delta$ and their derivatives $Q'$, $\alpha'$, and $\Delta'$ for $H_2$. The most reliable values for $Q$ are the theoretical values of Kolos and Wolniewicz (ref. 9), who tabulated $Q$ for a number of internuclear distances. From reference 9, $Q$ was found to be 0.45822 atomic units (au) (2.0556\times10^{-40} C m\(^2\)), and $Q'$ was found to be 0.5314 au (4.505\times10^{-30} C m). The most reliable values for $\alpha$ and $\Delta$ are the theoretical values of Kolos and Wolniewicz (ref. 10), who again tabulated values for a number of internuclear distances. From reference 10, $\alpha$ was found to be 5.1849 au (8.5482\times10^{-41} C^2m^2J^{-1}), $\alpha'$ was found to be 4.351 au (1.356\times10^{-30} C^2m J^{-1}), $\Delta$ was 1.8076 au (2.9801\times10^{-41} C^2m^2J^{-1}), and $\Delta'$ was 3.382 au (1.054\times10^{-30} C^2m J^{-1}). All these values are for an internuclear distance of 1.401446 bohr (0.741599\times10^{-10}\) m).

Using these values, the coefficients for the quadrupole-induced contributions to $\mu_{x_3}$ and $\mu_{x_3}'$ were calculated from equations (44) and (46) to (48) and are tabulated in table V. The quadrupole-induced contributions to $\mu_{x_3}$ and $\mu_{x_3}'$ for the five configura-

<table>
<thead>
<tr>
<th>Collision</th>
<th>Coefficient for quadrupole-induced contribution to component of dipole moment</th>
<th>Coefficient for quadrupole-induced contribution to derivative of component of dipole moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2-H_2$</td>
<td>$c_{00}$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$c_{20}$</td>
<td>3.9124</td>
</tr>
<tr>
<td></td>
<td>$c_{40}$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$g_{21}$</td>
<td>-2.2588</td>
</tr>
<tr>
<td>$H_2-H_2$</td>
<td>$d_{00}$</td>
<td>6.3749</td>
</tr>
<tr>
<td></td>
<td>$d_{20}$</td>
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<tr>
<td></td>
<td>$d_{20}$</td>
<td>0</td>
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<td></td>
<td>$d_{40}$</td>
<td>-2.2588</td>
</tr>
<tr>
<td>$H_2-H_2$</td>
<td>$d_{00}$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$d_{20}$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$d_{40}$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$h_{21}$</td>
<td>0</td>
</tr>
</tbody>
</table>
TABLE VI. COEFFICIENTS FOR QUADRUPOLE-INDUCED CONTRIBUTION
TO COMPONENTS OF DIPOLE MOMENT AND THEIR
DERIVATIVES FOR VARIOUS CONFIGURATIONS

<table>
<thead>
<tr>
<th>Collision</th>
<th>Configuration</th>
<th>Component</th>
<th>Coefficient for quadrupole-induced contribution to component of dipole moment</th>
<th>Coefficient for quadrupole-induced contribution to derivative of component of dipole moment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>au</td>
<td>C m^5</td>
</tr>
<tr>
<td>H_2-H_2</td>
<td>1</td>
<td>x_3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td>10.691</td>
<td>.71067 x 10^{-69}</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td></td>
<td>-10.691</td>
<td>-.71067</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H_2-H</td>
<td>1</td>
<td>x_1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>x_3</td>
<td>6.1860</td>
<td>.41121 x 10^{-69}</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>x_1</td>
<td>-3.0930</td>
<td>-.20560</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>x_3</td>
<td>1.5465</td>
<td>.10280</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>x_1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>x_3</td>
<td>-3.0930</td>
<td>-.20560 x 10^{-69}</td>
</tr>
</tbody>
</table>

^aCoefficients must be divided by R^4 to obtain the component of the dipole moment or its derivative.

Collisions were then calculated from equations (38) and (34), respectively. These are tabulated in table VI (the values given must be divided by R^4).

Total μ_3^x and μ'_3^x. - These totals were calculated from equations (40) and (41) for the five configurations and are plotted in figures 3 and 4. In general, they are strongly decreasing functions of intermolecular distance.

Comparison with other calculations. - Present results for μ_3^x (eq. (40)) and μ'_3^x (eq. (41)) are compared in figures 3 and 4 with other calculations for various configurations. In each figure, two other calculations are given: (1) an ab initio configuration-interaction calculation by Patch (ref. 11), and (2) a semiempirical overlap calculation (ref. 6 or 17) plus the same quadrupole-induced contributions as in this report. Use of the quadrupole-induced contributions of this report, which are based on references 9 and 10, and on equations (34), (38), (44), and (47), prevents older, obviously inaccurate calculations of the quadrupole-induced contributions from confusing the comparison. In figures 3, 4(a), and 4(c), all three calculations are in reasonable agreement between 4 and 5 bohr (2.117 x 10^{-10} and 2.646 x 10^{-10} m). The disagreement between the present
This report (eq. (40))
Patch (ref. 11)
Overlap contribution from ref. 17, quadrupole-induced contribution calculated from refs. 9 and 10 and from eqs. (38) and (44)

Figure 3. - $x_3$ component of dipole moment for $H_2-H_2$ configuration 3. Dipole moment of configuration 4 is the same except for sign. Configurations 1, 2, and 5 have no $x_3$ component of dipole moment.
This report (eq. (41))
Overlap contribution from ref. 6, quadrupole-induced contribution from refs. 9 and 10 and from eqs. (34) and (47).

Figure 4. - Derivative of $x_3$ component of dipole moment in $H_2-H_2$ collisions.
This report (eq. (41))

Patch (ref. 11)

Overlap contribution from
ref. 6, quadrupole induced
contribution from refs. 9
and 10 and from eqs. (34)
and (47)

(c) Planar perpendicular configuration 3.

(d) Planar perpendicular configuration 4.

Figure 4. - Concluded.
results and Patch's ab initio calculation at other values of $R$ has two causes: (1) the
ab initio calculation has insufficient allowance for electron correlation in the wave
function and no distortion of orbitals and, hence, is not valid for large $R$; and (2) the
present results do not include configuration interaction and hence are not valid for
small $R$. In figures 3, 4(a), and 4(c) the present results agree substantially with over-
lap calculations from reference 6 or 17 at all values of $R$.

In figures 4(b) and (d) the agreement of the three calculations is poor for all $R$
values. The reason is unknown. Fortunately, the magnitudes of $\mu'_{x3}$ in figures 4(b)
and (d) are only about one-half those in figures 4(a) and (c), so the lack of agreement be-
tween the present work and reference 11 is not too serious. The probable error should
be reduced by fairing the results together as discussed in the next section. In addition,
figures 4(b) and (d) show a disagreement between the present overlap contribution and
the overlap contribution from reference 6. This disagreement is principally due to the
different values of $\tilde{\zeta}$ used in calculating $\lambda$: 1.000 bohr$^{-1} \left(1.890 \times 10^{-10} \text{ m}^{-1}\right)$ in refer-
ence 6, and 1.174 bohr$^{-1} \left(2.219 \times 10^{-10} \text{ m}^{-1}\right)$ in the present work. The latter value is the
same as used for the orbitals in the $\text{H}_2$-$\text{H}_2$ calculation and is thus consistent. Also, it
gives better agreement with the measured integrated absorption coefficient of the funda-
mental as outlined in the following section.

Comparison with experiment. - The integrated absorption coefficient of a pressure-
induced vibrational transition may be said to vary roughly as the square of the derivative
of the dipole moment averaged over intermolecular distance. To provide a comparison
of the results in tables IV and V with experiment (ref. 18), the integrated absorption
coefficient of the $\text{H}_2$-$\text{H}_2$ pressure-induced fundamental vibrational transition was cal-
culated for a temperature of 298 K. The method of calculation was based on reference 6
with the following major changes:

(1) The $\text{H}_2$-$\text{H}_2$ average interaction energy was assumed to be a Morse potential
(ref. 19) for $R$ greater than 4 bohr ($2.117 \times 10^{-10}$ m). For $R$ less than 4 bohr, an ex-
ponential was fitted to the Morse potential at 4 bohr and an ab initio energy (ref. 11) at
2.5 bohr ($1.323 \times 10^{-10}$ m).

(2) $D_{2-222}$ and $D_{222-2}$ terms were included.

(3) Anharmonicity and vibration-rotation interaction were included, thereby re-
quiring $C_{2000}$.

(4) The quantities $\mu_{x3}$ and $\mu'_{x3}$ from reference 11 were used for $R$ between
2.5 and 4 bohr ($1.323 \times 10^{-10}$ and $2.117 \times 10^{-10}$ m). The quantities $\mu_{x3}$ and $\mu'_{x3}$ from
tables IV and V were used for $R$ between 6 and 8 bohr ($3.175 \times 10^{-10}$ and $4.233 \times 10^{-10}$ m).
Between 4 and 6 bohr the expansion coefficients for $\mu_{x3}$ and $\mu'_{x3}$ were fairied into re-
results from reference 11 at $R = 4$ bohr ($2.117 \times 10^{-10}$ m) and tables IV and V at $R = 6$ bohr.
(3.175x10^{-10} \text{ m}) by setting each expansion coefficient equal to \( f_1 R^{-4} + f_2 + f_3 R + f_4 R^2 \), where \( f_1 \) to \( f_4 \) are constants. This procedure was necessary for the reasons discussed in the preceding section. For \( R \) greater than 8 bohr (4.233x10^{-10} \text{ m}), there is little contribution to the absorption coefficient at 298 K, so the results of table IV were extrapolated and added to results from table V.

(5) Typographical errors were corrected.

(6) The \( x_1 \) and \( x_2 \) components of \( \vec{\mu} \) and \( \vec{\mu}' \) were neglected.

Using these assumptions, the integrated absorption coefficient of the fundamental was calculated to be 87 percent of the experimental value for the binary integrated absorption coefficient (ref. 18). The calculated value was low principally because the \( x_1 \) component of \( \vec{\mu}' \) was neglected (it was zero for the five configurations in fig. 2 but not for many others).

**Potential applications.** - The \( \text{H}_2-\text{H}_2 \) results in tables IV and V, together with results in references 11, 16, and 19 and available line shapes, are sufficient for calculations of \( \text{H}_2-\text{H}_2 \) pressure-induced vibrational, rotational, and translational absorption coefficients at temperatures up to 7000 K without recourse to the very dubious extrapolations and assumptions appearing in earlier work.

**DIPOLAR MOMENT AND ITS DERIVATIVE IN H_2-H COLLISIONS**

**Analysis**

Just as for \( \text{H}_2-\text{H}_2 \), the dipole moment of \( \text{H}_2-H \) and its derivative consist of two additive contributions: an overlap contribution and a quadrupole-induced contribution. The analysis is similar to that for \( \text{H}_2-\text{H}_2 \) except that (1) the repulsive distortion parameter \( \lambda \) is based on a repulsive H-H calculation using an orbital exponent \( \zeta \) which is the average of the orbital exponents for H and \( \text{H}_2 \), (2) the \( x_1 \) components of and \( \vec{\mu} \) and \( \vec{\mu}' \) are included as well as the \( x_3 \) components, (3) no molecular integrals are neglected, and (4) no series expansions in powers of \( \tau \) are used in evaluating molecular integrals because of the appreciable difference between \( \text{H}_2 \) and H orbital exponents. All equations are in atomic units (bohr, hartree, and electron charge).

**Coordinates.** - The coordinate system is shown in figure 5. The origin of the Cartesian coordinates \( x_1, x_2, \) and \( x_3 \) is on the intermolecular axis one-third of the way from molecule b-c to atom a. The relative position of the molecule is given by the polar angle \( \theta_1 \), and the molecule is always in the \( x_1-x_3 \) plane. Hence, the \( x_2 \) components of \( \vec{\mu} \) and \( \vec{\mu}' \) are zero, and \( \phi_1 \) is zero.
Overlap contribution to dipole moment. - For intermolecular distances of 4 bohr (2.117×10^{-10} m) or greater, it is reasonable to neglect configuration interaction, so the antisymmetric system wave function was assumed to be (ref. 20)

$$\Psi = \psi_1 - \psi_2$$  \hspace{1cm} (49)

where the determinantal wave functions $\psi_1$ and $\psi_2$ are given by

$$\psi_1 = (3!)^{-1/2} \det[a(1)\alpha(1), b(2)\beta(2), c(3)\alpha(3)]$$

$$\psi_2 = (3!)^{-1/2} \det[a(1)\alpha(1), b(2)\alpha(2), c(3)\beta(3)]$$  \hspace{1cm} (50)

The $x_j$ component of $\mu_a$ is given by

$$\mu_{ax_j} = \frac{-\int \Psi^2 \sum_{i=1}^{3} x_{ji} \, dV_1 \, dV_2 \, dV_3}{\int \Psi^2 \, dV_1 \, dV_2 \, dV_3} \hspace{1cm} (j = 1, 3)$$  \hspace{1cm} (51)
If equation (10) is assumed to hold, and integrals are defined as in equations (5) to (9) except for generalizing the subscript $j$ to $j$, equation (51) becomes

$$\mu_{ax_j} = \frac{N_{x_j}}{E} \quad (j = 1, 3)$$

(52)

where

$$N_{x_j} = -2\left(m_{ja} + m_{jb} + m_{jc} + 2m_{jbc}^2 + 2m_{jbc} \right) + 2\left(m_{jac}^2 + m_{jab}^2 + m_{jbc}^2 \right)$$

(53)

$$E = 2 + 2S_{bc}^2 - s_{ac}^2 - s_{ab}^2 - 2S_{bc} s_{ab} s_{ac}$$

(54)

As for $H_2-H_2$, Rosen-like orbitals were used:

$$a(i) = \left(\frac{\zeta_{a i}}{\pi}\right)^{1/2} e^{-\zeta_{a i} r^2} \left(1 + \lambda_{abi} \cos \theta_{abi} + \lambda_{ace} \cos \theta_{aci}\right)$$

(55)

$$b(i) = \left(\frac{\zeta_{bc i}}{\pi}\right)^{1/2} e^{-\zeta_{bc i} r^2} \left(1 + \kappa r_{bc i} \cos \theta_{bci} + \lambda_{ab i} \cos \theta_{bai}\right)$$

(56)

$$c(i) = \left(\frac{\zeta_{ac i}}{\pi}\right)^{1/2} e^{-\zeta_{ac i} r^2} \left(1 + \kappa r_{ac i} \cos \theta_{cbi} + \lambda_{ac i} \cos \theta_{cai}\right)$$

(57)

where $\zeta_{a}$ is the orbital exponent for the atom (1 bohr$^{-1}$ or $1.890 \times 10^{-10}$ m$^{-1}$) and $\kappa$ is the attractive distortion parameter for an isolated $H_2$ molecule with internuclear distance $r_{bc}$.

As for $H_2-H_2$, there are two kinds of overlap integrals. The integral $S_{bc}$ was evaluated by equations (18) and (19). Because of the appreciable difference between $H_2$ and $H$ orbital exponents $\zeta_{bc}$ and $\zeta_{a}$, respectively, integrals of type $s_{ac}$ were derived without truncated series expansions in powers of $\tau_{ac}$, where
The result is

\[
s_{ac} = \frac{1}{2} \left( \zeta_a \zeta_{bc} \right)^{3/2} r_{ac}^3 e^{-\sigma_{ac}} \left\{ 2M(\sigma_{ac}, \tau_{ac}) + r_{ac} \kappa \cos \theta_{cba} \left[ M(\sigma_{ac}, \tau_{ac}) + L(\sigma_{ac}, \tau_{ac}) \right] \right\}
\]

(57)

where

\[
\sigma_{ac} = \frac{1}{2} r_{ac} (\zeta_a + \zeta_{bc})
\]

(58)

\[
M(\sigma, \tau) = \frac{1}{4} \left[ A_1(\sigma) J_3(\sigma) - A_3(\tau) J_1(\sigma) \right]
\]

(59)

\[
L(\sigma, \tau) = \frac{1}{4} \left[ A_4(\sigma) J_2(\sigma) - A_2(\tau) J_4(\sigma) \right]
\]

(60)

\[
A_n(\tau) = -e^{-\frac{1}{\tau}} \left[ \frac{1}{\tau^2} + \frac{1}{\tau^3} + \frac{(n-1)(n-2)}{\tau^4} + \ldots + \frac{(n-1)!}{\tau^n} \right] \left[ 1 + \frac{(n-1)!}{\tau^n} \right]
\]

(61)

\[
J_n(\sigma) = \frac{(n-1)!}{\sigma^n} \left[ 1 + \sigma + \frac{\sigma^2}{2!} + \ldots + \frac{\sigma^{n-1}}{(n-1)!} \right]
\]

(62)

Integrals of type \( m_{jaa} \) were treated in a fashion similar to \( m_{3aa} \) for \( \text{H}_2-\text{H}_2 \), with the result

\[
m_{jaa} = \frac{2}{\zeta_a^2} \left( \lambda_{ab} \cos \theta_{abx_j} + \lambda_{ac} \cos \theta_{acx_j} \right) \quad (j = 1, 3)
\]

(63)

\[
m_{jbb} = \frac{2}{\zeta_{bc}^2} \left( \kappa \cos \theta_{bcx_j} - \lambda_{ab} \cos \theta_{abx_j} \right) \quad (j = 1, 3)
\]

(64)
The integral $m_{jcc}$ is similar to $m_{jbb}$.

The integral $m_{jbc}$ was derived just as for $H_2-H_2$.

$$m_{jbc} = \frac{1}{4} \zeta \, \chi_{bc} r_{bc}^5 e^{-\sigma_{bc}} \left\{ \lambda_{ab} \left[ \cos \theta_{bca} \cos \theta_{bcx_j} U(\sigma_{bc}) \right] + \sin \theta_{bca} \sin \theta_{bcx_j} \cos \varphi_{abcx_j} T(\sigma_{bc}) \right\} + \lambda_{ac} \left[ -\cos \theta_{cba} \cos \theta_{bcx_j} U(\sigma_{bc}) \right]$$

$$+ \sin \theta_{cba} \sin \theta_{bcx_j} \cos \varphi_{abcx_j} T(\sigma_{bc}) \right\} (j = 1, 3)$$

(65)

where $\sigma_{bc}$, $T(\sigma_{bc})$, and $U(\sigma_{bc})$ were found from equations (19), (28), and (29), respectively.

Just as for $s_{ac}$, integrals of type $m_{jac}$ were derived without series expansions in powers of $\tau_{ac}$.

$$m_{jac} = \frac{1}{4} \left( \xi \, \chi_{abc} \right)^{3/2} r_{ac}^5 e^{-\sigma_{ac}} \left[ -2 \cos \theta_{acx_j} L(\sigma_{ac}, \tau_{ac}) \left( \frac{1}{r_{ac}} + \lambda_{ac} \right) \right]$$

$$+ \kappa \left[ \cos \theta_{cba} \cos \theta_{acx_j} \left[ -U(\sigma_{ac}, \tau_{ac}) - L(\sigma_{ac}, \tau_{ac}) \right] \right]$$

$$+ \sin \theta_{cba} \sin \theta_{acx_j} \cos \varphi_{bacx_j} T(\sigma_{ac}, \tau_{ac}) \right\}$$

$$+ \lambda_{ab} \left[ \cos \theta_{abc} \cos \theta_{acx_j} \left[ U(\sigma_{ac}, \tau_{ac}) - L(\sigma_{ac}, \tau_{ac}) \right] \right]$$

$$+ \sin \theta_{abc} \sin \theta_{acx_j} \cos \varphi_{bacx_j} T(\sigma_{ac}, \tau_{ac}) \right\} (j = 1, 3)$$

(66)

where

$$T(\sigma, \tau) = \frac{1}{8} \left\{ J_5(\sigma) \left[ A_1(\tau) - A_3(\tau) \right] + J_3(\sigma) \left[ A_5(\tau) - A_1(\tau) \right] + J_1(\sigma) \left[ A_3(\tau) - A_5(\tau) \right] \right\}$$

(67)
and \( L(\sigma_{ac}, \tau_{ac}) \) is found from equation (60).

**Overlap contribution to derivative of dipole moment.** - In calculating the pressure-induced vibrational absorption, the partial derivative of \( \vec{\mu} \) with respect to the internuclear distance \( r_{bc} \) is necessary. If we let a prime indicate \( \partial/\partial r_{bc} \), from equation (52)

\[
\mu'_{ax_j} = \frac{N^*_x x_j}{E} - \frac{N^*_x E'}{E^2} \quad (j = 1, 3)
\]  

(69)

where \( N^*_x \) and \( E' \) were found by differentiating equations (53), (54), (57), (63) to (66), etc., analytically.

**Configurations and expansion coefficients.** - In calculating the pressure-induced vibrational absorption for \( \text{H}_2 \) colliding with an atom (ref. 21), \( \mu'_{x_3} \) is expanded in normalized Legendre polynomials \( \Theta_\ell_0(\theta) \)

\[
\mu'_{x_3} = \sum_{\ell=0}^{\infty} D_{\ell_0}(R) \Theta_\ell_0(\theta_1)
\]  

(70)

Figure 6. - Configurations used in calculations for \( \text{H}_2-H \) collisions. Intermolecular distance \( R \) had values from 4 to 8 bohr (2.117x10^{-10} m) to 4.233x10^{-10} m. The molecule had an internuclear distance of 1.40446 bohr (0.74599x10^{-10} m).
The fact that molecule b-c is homonuclear requires that \( \Theta_{i0} \) be zero when \( i \) is odd. In addition, calculations were restricted to the three configurations shown in figure 6. Thus, the only nonzero D's that could be determined were \( D_{00} \), \( D_{20} \), and \( D_{40} \). From equation (70) and figure 6

\[
\begin{align*}
\left( \mu_{x3}^{(1)} \right) &= \frac{1}{\sqrt{2}} D_{00} + \frac{\sqrt{10}}{2} D_{20} + \frac{3 \sqrt{2}}{2} D_{40} \\
\left( \mu_{x3}^{(2)} \right) &= \frac{1}{\sqrt{2}} D_{00} + \frac{\sqrt{10}}{8} D_{20} - \frac{39 \sqrt{2}}{64} D_{40} \\
\left( \mu_{x3}^{(3)} \right) &= \frac{1}{\sqrt{2}} D_{00} - \frac{\sqrt{10}}{4} D_{20} + \frac{9 \sqrt{2}}{16} D_{40}
\end{align*}
\]

Equations (71) were solved for the D's as follows:

\[
\begin{align*}
D_{00} &= \frac{\sqrt{2}}{15} \left( \mu_{x3}^{(1)} \right) + \frac{8 \sqrt{2}}{15} \left( \mu_{x3}^{(2)} \right) + \frac{2 \sqrt{2}}{5} \left( \mu_{x3}^{(3)} \right) \\
D_{20} &= \frac{20}{21 \sqrt{10}} \left( \mu_{x3}^{(1)} \right) + \frac{16}{21 \sqrt{10}} \left( \mu_{x3}^{(2)} \right) - \frac{12}{7 \sqrt{10}} \left( \mu_{x3}^{(3)} \right) \\
D_{40} &= \frac{32}{105 \sqrt{2}} \left( \mu_{x3}^{(1)} \right) - \frac{64}{105 \sqrt{2}} \left( \mu_{x3}^{(2)} \right) + \frac{32}{105 \sqrt{2}} \left( \mu_{x3}^{(3)} \right)
\end{align*}
\]

In calculating absorption coefficients it is convenient to take linear combinations of \( \mu_{x1} \) and \( \mu_{x2} \). For any configuration

\[
\begin{align*}
\mu(1) &= (2)^{-1/2} \left( \mu_{x1} + i \mu_{x2} \right), \quad \mu(-1) = (2)^{-1/2} \left( \mu_{x1} - i \mu_{x2} \right) \\
\mu'(1) &= (2)^{-1/2} \left( \mu_{x1}^' + i \mu_{x2}^' \right), \quad \mu'(1) = (2)^{-1/2} \left( \mu_{x1}^' - i \mu_{x2}^' \right)
\end{align*}
\]

(73)
where $i$ is the imaginary unit. For the configurations in figure 6, the $(1)$ and $(-1)$ components are equal. The quantity $\mu'(1)$ was expanded in spherical harmonics

$$
\mu'(1) = \sum_{l=0}^{\infty} \sum_{\mu=-l}^{l} \sqrt{2\pi} H_{l\mu}(r) Y_{l\mu}(\theta_1, \phi_1)
$$

(74)

Because of the symmetry and the three configurations considered, all of which have $\phi_1$, $\mu_{x_2}$, and $\mu'_{x_2}$ equal to zero and two of which have zero $\mu'(1)$, the only nonzero term in equation (74) that could be determined was

$$
H_{21} = \frac{4}{\sqrt{15}} \left( \mu'(1) \right)_2 = \frac{4}{\sqrt{30}} \left( \mu_{x_1} \right)_2
$$

(75)

In calculating pressure-induced translational or rotational absorption with any model, or pressure-induced vibrational absorption with anharmonicity and vibration-rotation interaction, $\mu'$ is needed, as well as $\mu'$. Hence, $\mu_{x_3}$ was expanded.

$$
\mu_{x_3} = \sum_{l=0}^{\infty} c_{l0}(r) \Theta_{l0}(\theta_1)
$$

(76)

which gave

$$
C_{00} = \frac{\sqrt{2}}{15} \left( \mu_{x_3} \right)_1 + \frac{8\sqrt{2}}{15} \left( \mu_{x_3} \right)_2 + \frac{2\sqrt{2}}{5} \left( \mu_{x_3} \right)_3
$$

$$
C_{20} = \frac{20}{21\sqrt{10}} \left( \mu_{x_3} \right)_1 + \frac{16}{21\sqrt{10}} \left( \mu_{x_3} \right)_2 - \frac{12}{7\sqrt{10}} \left( \mu_{x_3} \right)_3
$$

$$
C_{40} = \frac{32}{105\sqrt{2}} \left( \mu_{x_3} \right)_1 - \frac{64}{105\sqrt{2}} \left( \mu_{x_3} \right)_2 + \frac{32}{105\sqrt{2}} \left( \mu_{x_3} \right)_3
$$

(77)

Also, $\mu(1)$ was expanded

$$
\mu(1) = \sum_{l=0}^{\infty} \sum_{\mu=-l}^{l} \sqrt{2\pi} G_{l\mu}(r) Y_{l\mu}(\theta_1, \phi_1)
$$

(78)
The only nonzero term in equation (78) that could be determined from the three configurations was

\[ G_{21} = \frac{4}{\sqrt{15}} \left( \mu_1 \right)_2 = \frac{4}{\sqrt{30}} \left( \mu_{x_1} \right)_2 \]  \hspace{1cm} (79)

Although equations (70) to (79) were derived for \( \mu' \) and \( \mu \), they are linear and therefore equally applicable to the overlap and quadrupole-induced contributions to the expansion coefficients and components of \( \mu' \) and \( \mu \) just as for \( \text{H}_2-\text{H}_2 \).

**Quadrupole-induced contribution to dipole moment.** - The quadrupole-induced contribution to the dipole moment when a homonuclear diatomic molecule collides with an atom can be found from Colpa and Ketelaar's (ref. 15) equations for the electric field strength \( F \) due to a point quadrupole and the relation \( \mu = F \alpha_a \), where \( \alpha_a \) is the polarizability of an H atom. The expansion coefficients are

\[
\begin{align*}
C_{q00} &= 0 \\
C_{q20} &= 3 \sqrt{\frac{2}{5}} \frac{\alpha_a Q}{R^4} \\
C_{q40} &= 0 \\
G_{q21} &= -\sqrt{\frac{6}{5}} \frac{\alpha_a Q}{R^4}
\end{align*}
\]  \hspace{1cm} (80)

Equations (80) may be written

\[
\begin{align*}
C_{q00} &= \frac{c_{20}}{R^4} \\
C_{q20} &= \frac{g_{21}}{R^4}
\end{align*}
\]  \hspace{1cm} (81)

where each \( c_{20} \) and \( g_{21} \) are constants.
Quadrupole-induced contribution to derivative of dipole moment. - The expansion coefficients for these derivatives are found by differentiating equation (80)

\[
\begin{align*}
D_{q00} &= 0 \\
D_{q20} &= 3\sqrt{\frac{3}{5}} \frac{\alpha_a Q'}{R^4} \\
D_{q40} &= 0 \\
H_{q21} &= -\sqrt{\frac{6}{5}} \frac{\alpha_a Q'}{R^4}
\end{align*}
\]

Equations (82) may be written

\[
\begin{align*}
D_{q00} &= \frac{d_{q0}}{R^4} \\
D_{q20} &= \frac{h_{q21}}{R^4}
\end{align*}
\]

where each \(d_{q0}\) and \(h_{q21}\) are constants.

Results and Discussion

Repulsive distortion parameter. - This parameter was calculated just as for \(H_2-H_2\) except that \(\zeta\) was set equal to the average of the \(H_2\) and \(H\) values, namely 1.087 bohr\(^{-1}\) (2.054×10\(^{-10}\) m\(^{-1}\)). The resulting values of \(\lambda\) are given in table III.

Overlap contributions to \(\mu_{x_1}\) and \(\mu'_{x_1}\). - These contributions were calculated from equations (13) and (19), (28) and (29), (52) to (54), and (56) to (69) by using a digital computer. Values of the \(H_2\) equilibrium internuclear distance and \(\kappa, \kappa', \zeta_{bc},\) and \(\zeta'_{bc}\) were the same as used for \(H_2-H_2\), but, of course, \(\zeta_a\) was taken to be 1.000 bohr\(^{-1}\) (1.890×10\(^{-10}\) m\(^{-1}\)). The calculations were carried out for the three configurations in figure 6 and for
### TABLE VII. - EXPANSION COEFFICIENTS FOR COMPONENTS OF OVERLAP DIPOLE MOMENT IN H$_2$-H COLLISIONS

<table>
<thead>
<tr>
<th>Intermolecular distance, R (bohr m)</th>
<th>Expansion coefficients for components of overlap dipole moment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C$_{a00}$</td>
</tr>
<tr>
<td></td>
<td>C m</td>
</tr>
<tr>
<td>4.0</td>
<td>0.2117x10^{-5}</td>
</tr>
<tr>
<td>4.2</td>
<td>0.2223</td>
</tr>
<tr>
<td>4.4</td>
<td>0.2328</td>
</tr>
<tr>
<td>4.6</td>
<td>0.2434</td>
</tr>
<tr>
<td>4.8</td>
<td>0.2540</td>
</tr>
<tr>
<td>5.0</td>
<td>0.2646</td>
</tr>
<tr>
<td>5.2</td>
<td>0.2752</td>
</tr>
<tr>
<td>5.4</td>
<td>0.2858</td>
</tr>
<tr>
<td>5.6</td>
<td>0.2963</td>
</tr>
<tr>
<td>5.8</td>
<td>0.3069</td>
</tr>
<tr>
<td>6.0</td>
<td>0.3175</td>
</tr>
<tr>
<td>6.2</td>
<td>0.3281</td>
</tr>
<tr>
<td>6.4</td>
<td>0.3387</td>
</tr>
<tr>
<td>6.6</td>
<td>0.3493</td>
</tr>
<tr>
<td>6.8</td>
<td>0.3598</td>
</tr>
<tr>
<td>7.0</td>
<td>0.3704</td>
</tr>
<tr>
<td>7.2</td>
<td>0.3810</td>
</tr>
<tr>
<td>7.4</td>
<td>0.3916</td>
</tr>
<tr>
<td>7.6</td>
<td>0.4022</td>
</tr>
<tr>
<td>7.8</td>
<td>0.4128</td>
</tr>
<tr>
<td>8.0</td>
<td>0.4233</td>
</tr>
</tbody>
</table>
### TABLE VIII. - EXPANSION COEFFICIENTS FOR DERIVATIVES OF COMPONENTS OF OVERLAP DIPOLE MOMENT IN H₂-H COLLISIONS

<table>
<thead>
<tr>
<th>Intermolecular distance, ( R )</th>
<th>Expansion coefficients for derivatives of components of overlap dipole moment</th>
<th>( D_{a00} )</th>
<th>( D_{a20} )</th>
<th>( D_{a40} )</th>
<th>( H_{a21} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{bohr} )</td>
<td>( m )</td>
<td>( au )</td>
<td>( C )</td>
<td>( au )</td>
<td>( C )</td>
</tr>
<tr>
<td>4.0</td>
<td>( 0.2117 \times 10^{-9} )</td>
<td>( 0.3889 \times 10^{-1} )</td>
<td>( 0.6231 \times 10^{-20} )</td>
<td>( -0.0157 \times 10^{-1} )</td>
<td>( -0.0252 \times 10^{-20} )</td>
</tr>
<tr>
<td>4.2</td>
<td>( 0.2223 )</td>
<td>( 0.3001 )</td>
<td>( 0.4808 )</td>
<td>( -0.0149 )</td>
<td>( -0.0239 )</td>
</tr>
<tr>
<td>4.4</td>
<td>( 0.2328 )</td>
<td>( 0.2299 )</td>
<td>( 0.3683 )</td>
<td>( -0.0136 )</td>
<td>( -0.0218 )</td>
</tr>
<tr>
<td>4.6</td>
<td>( 0.2434 )</td>
<td>( 0.1748 )</td>
<td>( 0.2800 )</td>
<td>( -0.0121 )</td>
<td>( -0.0194 )</td>
</tr>
<tr>
<td>4.8</td>
<td>( 0.2540 )</td>
<td>( 0.1319 )</td>
<td>( 0.2113 )</td>
<td>( -0.0106 )</td>
<td>( -0.0170 )</td>
</tr>
<tr>
<td>5.0</td>
<td>( 0.2646 )</td>
<td>( 0.9868 \times 10^{-2} )</td>
<td>( 0.1584 )</td>
<td>( -0.0908 \times 10^{-2} )</td>
<td>( -0.0145 )</td>
</tr>
<tr>
<td>5.2</td>
<td>( 0.2752 )</td>
<td>( 0.7355 )</td>
<td>( 0.1178 )</td>
<td>( -0.0767 )</td>
<td>( -0.0123 )</td>
</tr>
<tr>
<td>5.4</td>
<td>( 0.2858 )</td>
<td>( 0.5433 )</td>
<td>( 0.8704 \times 10^{-21} )</td>
<td>( -0.0638 )</td>
<td>( -0.1022 \times 10^{-21} )</td>
</tr>
<tr>
<td>5.6</td>
<td>( 0.2963 )</td>
<td>( 0.3986 )</td>
<td>( 0.6386 )</td>
<td>( -0.0524 )</td>
<td>( -0.0840 )</td>
</tr>
<tr>
<td>5.8</td>
<td>( 0.3069 )</td>
<td>( 0.2904 )</td>
<td>( 0.4652 )</td>
<td>( -0.0426 )</td>
<td>( -0.0662 )</td>
</tr>
<tr>
<td>6.0</td>
<td>( 0.3175 )</td>
<td>( 0.2102 )</td>
<td>( 0.3368 )</td>
<td>( -0.0342 )</td>
<td>( -0.0546 )</td>
</tr>
<tr>
<td>6.2</td>
<td>( 0.3281 )</td>
<td>( 0.1511 )</td>
<td>( 0.2421 )</td>
<td>( -0.0273 )</td>
<td>( -0.0373 )</td>
</tr>
<tr>
<td>6.4</td>
<td>( 0.3387 )</td>
<td>( 0.1079 )</td>
<td>( 0.1729 )</td>
<td>( -0.0215 )</td>
<td>( -0.0344 )</td>
</tr>
<tr>
<td>6.6</td>
<td>( 0.3493 )</td>
<td>( 0.7657 \times 10^{-3} )</td>
<td>( 0.1227 )</td>
<td>( -0.1687 \times 10^{-3} )</td>
<td>( -0.0070 )</td>
</tr>
<tr>
<td>6.8</td>
<td>( 0.3598 )</td>
<td>( 0.5394 )</td>
<td>( 0.8642 \times 10^{-22} )</td>
<td>( -0.1312 )</td>
<td>( -0.2102 \times 10^{-22} )</td>
</tr>
<tr>
<td>7.0</td>
<td>( 0.3704 )</td>
<td>( 0.3776 )</td>
<td>( 0.6050 )</td>
<td>( -0.1013 )</td>
<td>( -0.1623 )</td>
</tr>
<tr>
<td>7.2</td>
<td>( 0.3810 )</td>
<td>( 0.2625 )</td>
<td>( 0.4206 )</td>
<td>( -0.0777 )</td>
<td>( -0.1245 )</td>
</tr>
<tr>
<td>7.4</td>
<td>( 0.3916 )</td>
<td>( 0.1811 )</td>
<td>( 0.2901 )</td>
<td>( -0.0592 )</td>
<td>( -0.0948 )</td>
</tr>
<tr>
<td>7.6</td>
<td>( 0.4022 )</td>
<td>( 0.1240 )</td>
<td>( 0.1987 )</td>
<td>( -0.0449 )</td>
<td>( -0.0719 )</td>
</tr>
<tr>
<td>7.8</td>
<td>( 0.4128 )</td>
<td>( 0.8415 \times 10^{-4} )</td>
<td>( 0.1348 )</td>
<td>( -0.3386 \times 10^{-4} )</td>
<td>( -0.0542 )</td>
</tr>
<tr>
<td>8.0</td>
<td>( 0.4233 )</td>
<td>( 0.5662 )</td>
<td>( 0.9071 \times 10^{-23} )</td>
<td>( -0.2541 )</td>
<td>( -0.4071 \times 10^{-23} )</td>
</tr>
</tbody>
</table>
Figure 7. $x_1$ and $x_3$ components of dipole moment in H$_2$-H collisions. The $x_1$ component of dipole moment is zero for linear configuration 1 and for isosceles configuration 3. Overlap and quadrupole-induced contributions are included.
intermolecular distances from 4 to 8 bohr \(2.117 \times 10^{-10}\) to \(4.233 \times 10^{-10}\) m). The expansion coefficients are tabulated in tables VII and VIII.

Quadrupole-induced contributions to \(\mu_{x_1}^t\) and \(\mu_{x_1}^{t'}\). - The same values of \(Q\) and \(Q'\) were used as for \(H_2-H_2\). The polarizability \(\alpha_a\) of the H atom was obtained from Pauling and Wilson (ref. 12) and had the value 4.5 au \(7.419 \times 10^{-41}\) C\(^2\) m\(^2\) J\(^{-1}\).

Using these values, the coefficients for the quadrupole-induced contributions to \(\mu_{x_1}, \mu_{x_3}, \mu_{x_1}^t,\) and \(\mu_{x_3}^t\) were calculated from equations (80) to (83) and are tabulated in table V. The quadrupole-induced contributions to \(\mu_{x_1}^t, \mu_{x_3}^t, \mu_{x_1}^{t'},\) and \(\mu_{x_3}^{t'}\) for the three configurations were then calculated from equations (71), (73), (74), (76), and (78) and are tabulated in table VI (the values given must be divided by \(R^4\)).

Total \(\mu_{x_1}, \mu_{x_3}, \mu_{x_1}^t,\) and \(\mu_{x_3}^t\). - These totals were found by summing the overlap and quadrupole-induced contributions for the three configurations and are plotted in figures 7 and 8. In general, their magnitudes are strongly decreasing functions of intermolecular distance.

![Graph](image)

Figure 8. - Derivatives of \(x_1\) and \(x_3\) components of dipole moment in \(H_2-H\) collisions. The derivative of the \(x_1\) component of dipole moment is zero for linear configuration 1 and isosceles configuration 3. Overlap and quadrupole-induced contributions are included.
Comparison with other investigations. - For the range of intermolecular distance used, there are no published theoretical or experimental values of $\mu$ or $\mu'$.

Potential applications. - No application is foreseen until ab initio calculations are made for $R$ less than 4 bohr ($2.117 \times 10^{-10}$ m). The semiempirical method in this report is not applicable for $R$ less than 4 bohr because it neglects configuration interaction. When used with ab initio calculations and a realistic average interaction energy (ref. 22), the $H_2-H$ results in tables V, VII, and VIII should make possible the calculation of the $H_2-H$ pressure-induced vibrational absorption coefficient. This coefficient has not previously been calculated.

CONCLUDING REMARKS

The electric dipole moment and its partial derivative with respect to $H_2$ internuclear distance were calculated for $H_2-H_2$ and $H_2-H$ collisions by using a semiempirical theory. Four planar configurations and one nonplanar configuration were employed for $H_2-H_2$. Three configurations were used for $H_2-H$. Intermolecular distances ranged from 4 to 8 bohr ($2.117 \times 10^{-10}$ to $4.233 \times 10^{-10}$ m). For intermolecular distances less than about 4 bohr, the semiempirical theory is not valid because of neglect of configuration interaction. To overcome this obstacle, the dipole moment and its derivative for $H_2-H_2$ from this report were faired into values from previous ab initio calculations for small intermolecular distances. The resulting integrated absorption coefficient at 298 K for the fundamental pressure-induced vibrational transition was 87 percent of the experimental value.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, May 19, 1970,
122-29.
Two sets of units are given for many symbols in this appendix: atomic units and SI units. In the atomic units, "charge" means "charge of an electron." In the text, tables, and figures, atomic units are frequently abbreviated au. All equations in the main text are in atomic units.

\( A_n(\tau)(n = 1, 2, \ldots, 5) \) functions of \( \tau \)

\( a(i)(i = 1, 2, 3, 4) \) orbital of electron \( i \) about proton \( a \), bohr \(-3/2\); m \(-3/2\)

\( b(i)(i = 1, 2, 3, 4) \) orbital of electron \( i \) about proton \( b \), bohr \(-3/2\); m \(-3/2\)

\( C_{al0}(\ell = 0, 2, 4) \) expansion coefficient for \( \mu_{ax_3} \) in \( H_2-H \) collision, charge bohr; C m

\( C_{al1}\mu_1^\ell 2\mu_2 \) expansion coefficient for \( \mu_{ax_3} \) in \( H_2-H_2 \) collision, charge bohr; C m

\( C_{i0}(\ell = 0, 2, 4) \) expansion coefficient for \( \mu_{x_3} \) in \( H_2-H \) collision, charge bohr; C m

\( C_{i1}\mu_1^\ell 2\mu_2 \) expansion coefficient for \( \mu_{x_3} \) in \( H_2-H_2 \) collision, charge bohr; C m

\( C_{ql0}(\ell = 0, 2, 4) \) expansion coefficient for \( \mu_{qx_3} \) in \( H_2-H \) collision, charge bohr; C m

\( C_{ql1}\mu_1^\ell 2\mu_2 \) expansion coefficient for \( \mu_{qx_3} \) in \( H_2-H_2 \) collision, charge bohr; C m

\( c(i)(i = 1, 2, 3, 4) \) orbital of electron \( i \) about proton \( c \), bohr \(-3/2\); m \(-3/2\)

\( c_{i0}(\ell = 0, 2, 4) \) coefficient for quadrupole-induced contribution to \( x_3 \) component of dipole moment in \( H_2-H \) collision, charge bohr\(^5\); C m\(^5\)

\( c_{i1}\mu_1^\ell 2\mu_2 \) coefficient for quadrupole-induced contribution to \( x_3 \) component of dipole moment in \( H_2-H_2 \) collision, charge bohr\(^5\); C m\(^5\)

\( D_{al0}(\ell = 0, 2, 4) \) expansion coefficient for \( \mu''_{ax_3} \) in \( H_2-H \) collision, charge; C

\( D_{al1}\mu_1^\ell 2\mu_2 \) expansion coefficient for \( \mu''_{ax_3} \) in \( H_2-H_2 \) collision, charge; C
D_{l0}(l = 0, 2, 4) expansion coefficient for \( \mu_x \) in \( \text{H}_2-\text{H} \) collision, charge; \( \text{C} \)

D_{l1} \mu_{l2} \mu_2 expansion coefficient for \( \mu_x \) in \( \text{H}_2-\text{H}_2 \) collision, charge; \( \text{C} \)

D_{q1} \mu_{l2} \mu_2 expansion coefficient for \( \mu_{qx} \) in \( \text{H}_2-\text{H}_2 \) collision, charge; \( \text{C} \)

d(i)(i = 1, 2, 3, 4) orbital of electron \( i \) about proton \( d \), bohr \(^{-3/2} \); m \(^{-3/2} \)

d_{l0}(l = 0, 2, 4) coefficient for quadrupole-induced contribution to \( x_3 \) component of derivative of dipole moment in \( \text{H}_2-\text{H} \) collision, charge bohr \(^4 \); \( \text{C m}^4 \)

d_{l1} \mu_{l2} \mu_2 coefficient for quadrupole-induced contribution to \( x_3 \) component of derivative of dipole moment in \( \text{H}_2-\text{H}_2 \) collision, charge bohr \(^4 \); \( \text{C m}^4 \)

dV_{l1}(i = 1, 2, 3, 4) element of volume for electron \( i \) in configuration space and spin space, bohr \(^3 \); m \(^3 \)

dV_{l1} element of volume for electron \( l \) in configuration space, bohr \(^3 \); m \(^3 \)

E denominator of expression for component of dipole moment

\( \overrightarrow{F} \) electric field strength vector, hartree bohr \(^{-1} \) charge \(^{-1} \); J m \(^{-1} \) C \(^{-1} \)

f_{l1}(i = 1, 2, 3, 4) constants for fairing of expansion coefficients

G_{a21} expansion coefficient for overlap contribution to \( \mu \) component of dipole moment, charge bohr, \( \text{C m} \)

G_{l, \mu} expansion coefficient for \( \mu \) component of dipole moment, charge bohr; \( \text{C m} \)

G_{q21} expansion coefficient for quadrupole-induced contribution to \( \mu \) component of dipole moment, charge bohr; \( \text{C m} \)

G_{q21} expansion coefficient for quadrupole-induced contribution to \( (1) \) component of dipole moment, charge bohr \(^5 \); C m \(^5 \)

J_{a21} expansion coefficient for overlap contribution to \( \mu \) component of dipole moment, charge bohr; \( \text{C m} \)

J_{l, \mu} expansion coefficient for \( \mu \) component of dipole moment, charge bohr; \( \text{C m} \)

J_{q21} expansion coefficient for quadrupole-induced contribution to \( \mu \) component of dipole moment, charge; \( \text{C m} \)

h_{21} coefficient for quadrupole-induced contribution to \( (1) \) component of derivative of dipole moment, charge bohr \(^4 \); C m \(^4 \)
$\hbar$ Planck constant divided by $2\pi$, J/sec

$J_n(\sigma)(n = 1, 2, \ldots, 5)$ function of $\sigma$

$L(\sigma, \tau)$ function of $\sigma$ and $\tau$

$M(\sigma)$ approximation to $M(\sigma, \tau)$ for small $\tau$

$M(\sigma, \tau)$ function of $\sigma$ and $\tau$

$m_{jaa}(j = 1, 3)$ integral of square of orbital $a(1)$ and $x_{ja1}$, bohr; m

$m_{jab}(j = 1, 3)$ integral of orbitals $a(1)$ and $b(1)$, and $x_{jab1}$, bohr; m

$N_{x_j}$ numerator of expression for $\mu_{x_j}$ for $H_2$-$H$, charge bohr; C m

$N_1, N_2, N_3$ contributions to numerator of expression for $\mu_{x_3}$ for $H_2$-$H_2$, charge bohr; C m

$Q, Q_{ab}, Q_{cd}$ scalar quadrupole moment of $H_2$ molecule (subscripts indicate which molecule), charge bohr$^2$; C m$^2$

$Q_{XX}, Q_{YY}, Q_{ZZ}$ elements of $H_2$ quadrupole moment tensor, charge bohr$^2$; C m$^2$

$R$ internuclear distance, bohr; m

$r$ internuclear distance, bohr; m

$r_{ab}$ distance from proton $a$ to proton $b$, bohr; m

$r_{a1}$ distance from proton $a$ to electron $1$, bohr; m

$S_{ab}$ overlap integral for orbitals $a(1)$ and $b(1)$ (in same molecule)

$s_{ac}$ overlap integral for orbitals $a(1)$ and $c(1)$ (in different molecules)

$T(\sigma)$ approximation to $T(\sigma, \tau)$ for small $\tau$

$T(\sigma, \tau)$ function of $\sigma$ and $\tau$

$U(\sigma)$ approximation to $U(\sigma, \tau)$ for small $\tau$

$U(\sigma, \tau)$ function of $\sigma$ and $\tau$

$X, Y, Z$ Cartesian coordinates with origin at midpoint of line connecting protons $a$ and $b$ and with $Z$ running along line $ab$, bohr; m

$x_j(j = 1, 2, 3)$ Cartesian coordinates (see figs. 1 and 5), bohr; m

$x_{ji}(j = 1, 3)$ $x_j$ coordinate of electron $i$, bohr; m
\( x_{3a1} \) component of vector from proton a to electron 1, bohr; m

\( x_{3ac1} \) component of vector from center of line ac to electron 1, bohr; m

\( x_{3p} \) coordinate of proton p, bohr; m

\( Y_{\ell \mu} \) spherical harmonic

\( \alpha(i)(i = 1, 2, 3, 4) \) spin eigenfunction of electron i with component of spin angular momentum along axis of quantization equal to \( \hbar/2 \)

\( \alpha_a \) polarizability of H atom a, charge \( \text{bohr}^2 \) \( \text{hartree}^{-1} \); \( C\text{ m}^2 J^{-1} \)

\( \alpha_a, \alpha_{ab}, \alpha_{cd} \) average polarizability of \( \text{H}_2 \) molecule (subscripts indicate which molecule), charge \( \text{bohr}^2 \) \( \text{hartree}^{-1} \); \( C\text{ m}^2 J^{-1} \)

\( \beta(i)(i = 1, 2, 3, 4) \) spin eigenfunction of electron i with component of spin angular momentum along axis of quantization equal to \( -\hbar/2 \)

\( \Delta, \Delta_{ab}, \Delta_{cd} \) anisotropy of polarizability of \( \text{H}_2 \) molecule (subscripts indicate which molecule), charge \( \text{bohr}^2 \) \( \text{hartree}^{-1} \); \( C\text{ m}^2 J^{-1} \)

\( \zeta_a \) orbital exponent of H atom a, \( \text{bohr}^{-1} \); \( m^{-1} \)

\( \zeta_a, \zeta_{ab}, \zeta_{bc}, \zeta_{cd} \) orbital exponent of \( \text{H}_2 \) molecule (subscripts indicate which molecule), \( \text{bohr}^{-1} \); \( m^{-1} \)

\( \bar{\zeta} \) orbital exponent of two repelling H atoms used in calculating \( \lambda \), \( \text{bohr}^{-1} \); \( m^{-1} \)

\( \Theta_{\ell \mu} \) normalized associated Legendre function

\( \theta, \theta_1, \theta_2 \) polar angles (see figs. 1 and 5), deg

\( \theta_{abc} \) angle between protons b and c at proton a (first or second quadrant), deg

\( \theta_{abx_j}(i = 1, 3) \) angle at proton a between proton b and line through proton a parallel to the \( x_j \) axis (first or second quadrant), deg

\( \theta_{ab1} \) angle between proton b and electron 1 at proton a (first or second quadrant), deg

\( \kappa, \kappa_{ab}, \kappa_{cd} \) attractive distortion parameter of \( \text{H}_2 \) molecule (subscripts indicate which molecule), \( \text{bohr}^{-1} \); \( m^{-1} \)

\( \lambda, \lambda_{ab} \) repulsive distortion parameter (subscripts indicate repelling orbitals), \( \text{bohr}^{-1} \); \( m^{-1} \)

\( \bar{\mu} \) dipole moment vector, charge bohr; C m
\( \bar{\mu}_a \) overlap contribution to \( \bar{\mu} \), charge bohr; C m

\( \mu_{ax_j} (j = 1, 2, 3) \) x\(_j\) component of \( \bar{\mu}_a \), charge bohr; C m

\( \mu_{qx_3} \) x\(_3\) component of quadrupole-induced contribution to \( \bar{\mu} \), charge bohr; C m

\( \mu_{x_j} (j = 1, 2, 3) \) x\(_j\) component of \( \bar{\mu} \), charge bohr; C m

\( \mu(1), \mu(-1) \) complex components of \( \bar{\mu} \), charge bohr; C m

\( \sigma \) \( \sigma_{ac} \) with any subscripts

\( \sigma_{ac} \) \( r_{ac} \) times average value of \( \zeta \) for orbitals \( a(1) \) and \( c(1) \)

\( \tau \) \( \tau_{ac} \) with any subscripts

\( \tau_{ac} \) function of \( r_{ac} \) and difference of orbital exponents of orbitals \( a(1) \) and \( c(1) \)

\( \varphi, \varphi_1, \varphi_2 \) azimuthal angles (see figs. 1 and 5), deg

\( \omega_{cabx_j} (j = 1, 3) \) dihedral angle between plane \( cab \) and plane containing \( a, b, \) and line parallel to the \( x_j \) axis, deg

\( \Psi \) antisymmetric system wave function, bohr\(^{-6}\); m\(^{-6}\)

\( \psi_i (i = 1, 2, \ldots, 5) \) determinantal wave function, bohr\(^{-6}\); m\(^{-6}\)

Subscript:

( )_i configuration \( i \) (figs. 2 and 6)

Superscript:

' indicates partial differentiation with respect to internuclear distance of left-hand molecule (figs. 1 and 5)
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