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SEMIEMPIRICAL ELECTRIC DIPOLE MOMENT AND ITS DERIVATIVE IN H_2-H_2 AND H_2-H COLLISIONS

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16. Abstract

The dipole moment and its derivative with respect to H_2 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 H_2-H_2 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 H_2-H_2 both contributions were improved. For H_2-H they were reformulated. For H_2-H_2 four planar configurations and one nonplanar configuration were used and substantial agreement with infrared absorption was obtained. For H_2-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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SUMMARY

In a gas, when two H_2 molecules or an H_2 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 H_2 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 H_2-H_2 and H_2-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 H_2-H_2 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 H_2-H_2 the overlap analysis was improved, and for H_2-H it was reformulated. For both contributions the only experimental input was the equilibrium internuclear distance of H_2, which was obtained from spectroscopic data.

Dipole moment and its derivative were calculated for a number of collision configurations. For H_2-H_2 four planar configurations and one nonplanar configuration were used. For H_2-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 H_2-H_2 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 H_2 molecules with various collision partners. In the cases mentioned, important collision partners include H_2 and He and probably H. No experimental data taken much above room temperature exist for collision partners H_2 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 H_2 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 H_2 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 H_2, or both, must change. If only the relative kinetic energy changes, the process is called pressure-induced translational absorption. If the H_2 rotational energy changes but not the vibrational energy, the process is termed pressure-induced rotational absorption. If the H_2 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 H_2 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 H_2. If the collision partner is a homonuclear diatomic molecule, its quadrupole moment may also induce a dipole moment in H_2. 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 H_2 internuclear 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 H_2. Van Kranendonk and Bird (ref. 5) gave a semiempirical theory for the overlap contribution in H_2-H_2 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 Krandendonk 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 H_2 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 H_2-H_2, 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 H_2-H absorption have been made.

This report calculates dipole moments and their derivatives for H_2-H_2 and H_2-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 H_2-H_2 and had to be reformulated for H_2-H.

The main body of the report is divided into two parts: one for H_2-H_2 and for H_2-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 H_2-H_2 investigations, limitations, and potential applications.

DIPOLE MOMENT AND ITS DERIVATIVE IN H_2-H_2 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 H_2-H_2 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 λ 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

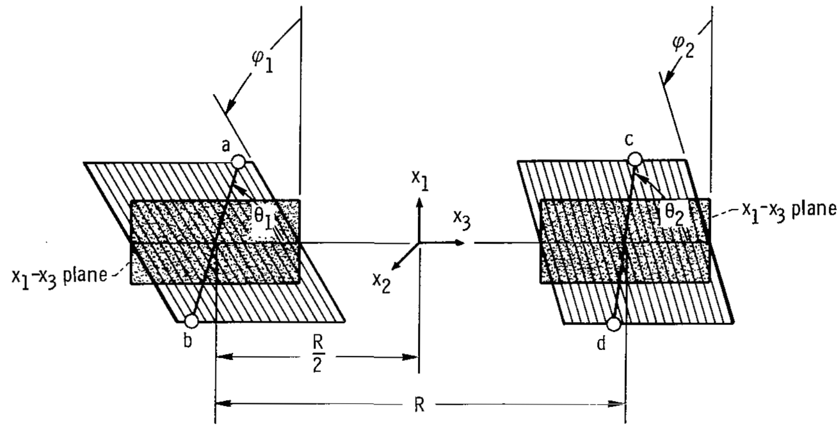


Figure 1. - Coordinates in H_2-H_2 collisions. The molecules are a-b and c-d; protons are at a, b, c, and d; the x_3 axis passes through the midpoints of the molecules; θ_1 and θ_2 are polar angles; φ_1 and φ_2 are azimuthal angles measured in the x_1-x_2 plane.

molecules a-b and c-d (symbols are given in the appendix). The relative positions of the molecules are given by polar angles angles θ_1 and θ_2 and azimuthal angles φ_1 and φ_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 (2.117×10^{-10} m) or greater, it is reasonable to neglect configuration interaction, so the antisymmetric system wave function Ψ was assumed to be

$$\Psi = \psi_1 - \psi_3 - \psi_4 + \psi_5 \tag{1}$$

where the determinantal wave functions ψ_1 and ψ_3 to ψ_5 are given by

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

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 $\vec{\mu}_a$ is given by

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

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

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

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:

$$S_{ab} \equiv \int a(1)b(1)dv_1 \qquad \text{(a and b in same molecule)} \tag{5}$$

$$s_{ac} \equiv \int a(1)c(1)dv_1 \qquad \text{(a and c in different molecules)} \tag{6}$$

$$m_{3aa} \equiv \int a^2(1)x_{3a1}dv_1 \tag{7}$$

$$m_{3ab} \equiv \int a(1)b(1)x_{3ab1}\,dv_1 \qquad \text{(a and b in same molecule)} \tag{8}$$

$$m_{3ac} \equiv \int a(1)c(1)x_{3ac1}\,dv_1 \qquad \text{(a and c in different molecules)} \tag{9}$$

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 $\overline{ac}$ to electron 1, and dv_1 is an element of volume for electron 1. In addition, it was assumed that

$$\int a^2(1)dv_1 = 1 \tag{10}$$

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

$$\mu_{ax_3} = \frac{N_1 + N_2 + N_3}{E} \tag{11}$$

where

$$N_1 \equiv -4\left[(m_{3aa} + m_{3bb} + 2m_{3ab}S_{ab})\left(1 + S_{cd}^2\right) + (m_{3cc} + m_{3dd} + 2m_{3cd}S_{cd})\left(1 + S_{ab}^2\right)\right] \tag{12}$$

$$N_2 \equiv 4\Big[m_{3ac}(s_{ac} + S_{ab}s_{bc} + S_{cd}s_{ad} + S_{ab}S_{cd}s_{bd}) + m_{3ad}(s_{ad} + S_{ab}s_{bd} + S_{cd}s_{ac} + S_{ab}S_{cd}s_{bc}) + m_{3bc}(s_{bc} + S_{ab}s_{ac} + S_{cd}s_{bd} + S_{ab}S_{cd}s_{ad}) + m_{3bd}(s_{bd} + S_{ab}s_{ad} + S_{cd}s_{bc} + S_{ab}S_{cd}s_{ac})\Big] \tag{13}$$

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

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

In equations (14) and (15), terms of order s^3 and s^4 were neglected because they were found to have negligible effect on μ_{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

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

where θ_{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, κ_{ab} is an attractive distortion parameter (always positive) for an isolated H_2 molecule a-b, and λ_{ac} is a repulsive distortion parameter (always negative) for the two repelling atoms a and c. The terms in equation (16) containing κ_{ab}, λ_{ac}, and λ_{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 κ^2, $\kappa\lambda$, and λ^2 are neglected, equation (10) is satisfied. The orbital exponent ζ_{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 κ_{ab}, λ_{ac}, and λ_{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 λ_{ac} was calculated by a variational method for two repelling H atoms a and c by assuming orbitals of the form

$$a(1) = \left(\frac{\bar{\zeta}^3}{\pi}\right)^{1/2} e^{-\bar{\zeta} r_{a1}}(1 + \lambda_{ac} r_{a1} \cos \theta_{ac1}) \tag{17}$$

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 $\bar{\zeta}$ and λ_{ac} were optimized. In our version this would cause $\bar{\zeta} \neq \zeta_{ab}$. To avoid this in calculating λ_{ac} for use with H_2-H_2, $\bar{\zeta}$ 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 $\zeta_{ab} \neq \zeta_{cd}$ 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 $\kappa\lambda$, κ^2, λ^2, and λ were neglected compared to terms containing κ.

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

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

where

$$\sigma_{ab} \equiv \zeta_{ab} r_{ab} \tag{19}$$

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

$$\sigma_{ac} \equiv \frac{1}{2} r_{ac}(\zeta_{ab} + \zeta_{cd}) \tag{20}$$

$$\tau_{ac} \equiv \frac{1}{2} r_{ac}(\zeta_{ab} - \zeta_{cd}) \tag{21}$$

Then

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

$$\left.\left. + \kappa_{cd} \cos \theta_{cda}\left[M(\sigma_{ac}) + L(\sigma_{ac}, \tau_{ac})\right]\right\}\right) \tag{22}$$

where

$$M(\sigma) \equiv \frac{1}{\sigma^3} + \frac{1}{\sigma^2} + \frac{1}{3\sigma} \tag{23}$$

$$L(\sigma,\tau) \equiv \left(\frac{1}{\sigma^4} + \frac{1}{\sigma^3} + \frac{2}{5\sigma^2} + \frac{1}{15\sigma}\right)\tau \tag{24}$$

and where, after integration, exponentials with arguments $\pm\tau_{ac}$ were expanded in power series, and then terms of order τ_{ac}^2 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 κ^2, $\kappa\lambda$, and λ^2 were neglected. It was necessary to use the law of cosines from spherical trigonometry to get

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

where θ_{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 κ^2, $\kappa\lambda$, and λ^2 were neglected. The relation

$$x_{3ab1} = \frac{x_{3a1} + x_{3b1}}{2} \tag{26}$$

was needed. The result was

$$m_{3ab} = \frac{1}{4}\zeta_{ab}^{3} r_{ab}^{5} e^{-\sigma_{ab}} \Bigg\{ \lambda_{ac}\Big[\cos\theta_{abc}\cos\theta_{abx_3} U(\sigma_{ab})$$

$$+ \sin\theta_{abc}\sin\theta_{abx_3}\cos\varphi_{cabx_3} T(\sigma_{ab})\Big] + \lambda_{ad}\Big[\cos\theta_{abd}\cos\theta_{abx_3} U(\sigma_{ab})$$

$$+ \sin\theta_{abd}\sin\theta_{abx_3}\cos\varphi_{dabx_3} T(\sigma_{ab})\Big] + \lambda_{bc}\Big[-\cos\theta_{bac}\cos\theta_{abx_3} U(\sigma_{ab})$$

$$+ \sin\theta_{bac}\sin\theta_{abx_3}\cos\varphi_{cabx_3} T(\sigma_{ab})\Big] + \lambda_{bd}\Big[-\cos\theta_{bad}\cos\theta_{abx_3} U(\sigma_{ab})$$

$$+ \sin\theta_{bad}\sin\theta_{abx_3}\cos\varphi_{dabx_3} T(\sigma_{ab})\Big]\Bigg\} \tag{27}$$

where φ_{cabx_3} is the dihedral angle between plane cab and a plane containing the line $\overline{ab}$ and the x_3 axis and where

$$T(\sigma) \equiv \frac{4}{\sigma^5} + \frac{4}{\sigma^4} + \frac{8}{5\sigma^3} + \frac{4}{15\sigma^2} \tag{28}$$

$$U(\sigma) \equiv \frac{4}{\sigma^5} + \frac{4}{\sigma^4} + \frac{9}{5\sigma^3} + \frac{7}{15\sigma^2} + \frac{1}{15\sigma} \tag{29}$$

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

$$m_{3ac} = \frac{1}{4}\left(\zeta_{ab}\zeta_{cd}\right)^{3/2} r_{ac}^{5} e^{-\sigma_{ac}}\Bigg(-2\cos\theta_{acx_3} L(\sigma_{ac},\tau_{ac})\left(\frac{1}{r_{ac}} + \lambda_{ac}\right)$$

$$+ \kappa_{ab}\left\{\cos\theta_{abc}\cos\theta_{acx_3}\left[U(\sigma_{ac}) - L(\sigma_{ac},\tau_{ac})\right] + \sin\theta_{abc}\sin\theta_{acx_3}\cos\varphi_{bacx_3}T(\sigma_{ac})\right\}$$

$$+ \kappa_{cd}\left\{\cos\theta_{cad}\cos\theta_{acx_3}\left[-U(\sigma_{ac}) - L(\sigma_{ac},\tau_{ac})\right] + \sin\theta_{cad}\sin\theta_{acx_3}\cos\varphi_{dacx_3}T(\sigma_{ac})\right\}$$

$$+ \lambda_{ad}\left\{\cos\theta_{acd}\cos\theta_{acx_3}\left[U(\sigma_{ac}) - L(\sigma_{ac},\tau_{ac})\right] + \sin\theta_{acd}\sin\theta_{acx_3}\cos\varphi_{dacx_3}T(\sigma_{ac})\right\}$$

$$+ \lambda_{bc}\Bigg\{\cos\theta_{cab}\cos\theta_{acx_3}\left[-U(\sigma_{ac}) - L(\sigma_{ac},\tau_{ac})\right]$$

$$+ \sin\theta_{cab}\sin\theta_{acx_3}\cos\varphi_{bacx_3}T(\sigma_{ac})\Bigg\}\Bigg) \tag{30}$$

where, after integration, exponentials with arguments $\pm\tau_{ac}$ were expanded in power series and then terms of order τ_{ac}^2 and higher were neglected. The angle φ_{bacx_3} is the dihedral angle between plane bac and a plane containing line $\overline{ac}$ 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)

$$\mu'_{ax_3} = \frac{N'_1 + N'_2 + N'_3}{E} - \frac{(N_1 + N_2 + N_3)E'}{E^2} \tag{31}$$

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. In general, in taking the derivative with respect to r_{ab} it should be noted that ζ_{ab}, κ_{ab}, r_{ac}, r_{ad}, r_{bc}, r_{bd}, λ_{ac}, λ_{ad}, λ_{bc}, λ_{bd}, and most of the θ's and φ'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 μ'_{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

	Van Kranendonk and Bird (ref. 5)	Britton and Crawford (ref. 6)	This report
Antisymmetric system wave function, Ψ	No	Yes	Yes
Only x_3 component of $\vec{\mu}'_a$	Yes	Yes	Yes
Type m_{3ac} integrals, as well as type m'_{3ac}, retained in N'_2	No	No	Yes
N'_3 included in μ'_{ax_3}	No	No	Yes
Terms of order s^2 retained in final expression for E	No	No	Yes
$(N_1 + N_2 + N_3)E'/E^2$ retained in μ'_{ax_3}	No	No	Yes
Value of orbital exponent $\bar{\zeta}$ in calculation of λ, $bohr^{-1}$ (m^{-1})	1.000 (1.890×10^{10})	1.000 (1.890×10^{10})	1.174 (2.219×10^{10})
Factor of $1 + \kappa r$ in integrals of type S_{ab}	No	Yes	Yes
Complete expression for integrals of type m_{3ac} and m'_{3ac}, except for neglect of terms of order τ^2_{ac} and higher	No	No	Yes
r'_{ac}, r'_{ad}, r'_{bc}, and r'_{bd} included in derivatives of integrals	No	No	Yes
λ' included in derivatives of integrals	No	No	Yes
θ' and φ' (with letter subscripts) included in derivatives of integrals	No	No	Yes
Number of planar configurations included	4	4	4
Number of nonplanar configurations included	1	0	1
Equilibrium internuclear distance of H_2 molecules, bohr(m)	[a]1.416 (0.7493×10^{-10})	[a]1.416 (0.7493×10^{-10})	[b]1.401446 (0.741599×10^{-10})
D_{2-222} and D_{222-2} included in μ'_{ax_3} expansion	No	No	Yes

[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, μ'_{x_3} is always expanded in spherical harmonics Y_{lu} (refs. 5 and 6).

$$\mu'_{x_3} = \sum_{l_1=0}^{\infty} \sum_{\mu_1=-l_1}^{l_1} \sum_{l_2=0}^{\infty} \sum_{\mu_2=-l_2}^{l_2} 2\pi D_{l_1\mu_1 l_2\mu_2}(R) Y_{l_1\mu_1}(\theta_1, \varphi_1) Y_{l_2\mu_2}(\theta_2, \varphi_2) \tag{32}$$

where

$$Y_{l\mu}(\theta, \varphi) \equiv (2\pi)^{-1/2} \Theta_{l\mu}(\theta) e^{i\mu\varphi} \tag{33}$$

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},

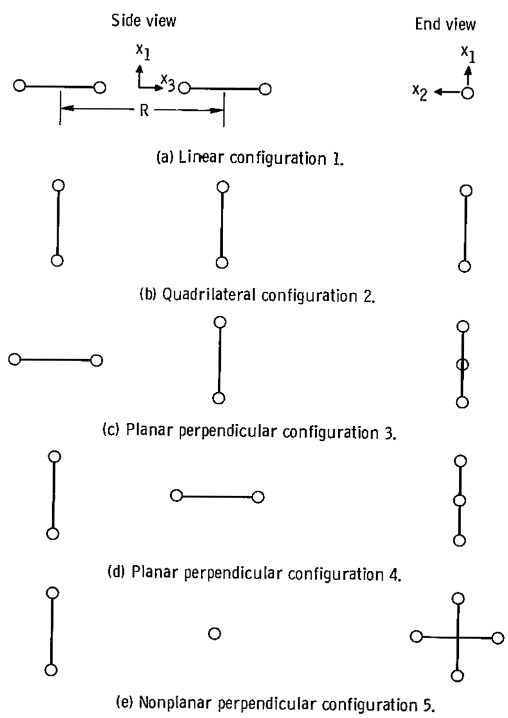


Figure 2. - Configurations used in calculations for H_2-H_2 collisions. Intermolecular distance R had values from 4 to 8 bohr (2.117×10^{-10} to 4.233×10^{-10} m). The molecules all had internuclear distances of 1.401446 bohr (0.741599×10^{-10} m), which is the equilibrium value (ref. 16).

TABLE II. - POLAR AND AZIMUTHAL ANGLES FOR FIVE

CONFIGURATIONS SHOWN IN FIGURE 2

Configuration	Polar angle of molecule a-b, θ_1, deg	Polar angle of molecule c-d, θ_2, deg	Azimuthal angle of molecule a-b, φ_1, deg	Azimuthal angle of molecule c-d, φ_2, deg
1	0	0	0	0
2	90	90	↓	↓
3	0	90		
4	90	0		
5	90	90		90

D_{0020}, D_{2020}, D_{2-222} and D_{222-2} (the last two are equal). Let $\left(\mu'_{x_3}\right)_i$ be μ'_{x_3} for the ith configuration. Then from equations (32) and (33) and table II,

$$\left.\begin{aligned}
\left(\mu'_{x_3}\right)_1 &= \frac{1}{2} D_{0000} + \sqrt{\frac{5}{4}} D_{2000} + \sqrt{\frac{5}{4}} D_{0020} + \frac{5}{2} D_{2020} \\
\left(\mu'_{x_3}\right)_2 &= \frac{1}{2} D_{0000} - \sqrt{\frac{5}{16}} D_{2000} - \sqrt{\frac{5}{16}} D_{0020} + \frac{5}{8} D_{2020} + \frac{15}{8} D_{2-222} \\
\left(\mu'_{x_3}\right)_3 &= \frac{1}{2} D_{0000} + \sqrt{\frac{5}{4}} D_{2000} - \sqrt{\frac{5}{16}} D_{0020} - \frac{5}{4} D_{2020} \\
\left(\mu'_{x_3}\right)_4 &= \frac{1}{2} D_{0000} - \sqrt{\frac{5}{16}} D_{2000} + \sqrt{\frac{5}{4}} D_{0020} - \frac{5}{4} D_{2020} \\
\left(\mu'_{x_3}\right)_5 &= \frac{1}{2} D_{0000} - \sqrt{\frac{5}{16}} D_{2000} - \sqrt{\frac{5}{16}} D_{0020} + \frac{5}{8} D_{2020} - \frac{15}{8} D_{2-222}
\end{aligned}\right\} \qquad (34)$$

where the equality of D_{2-222} and D_{222-2} was invoked. Equations (34) were solved for D

$$\left.\begin{aligned}
D_{0000} &= \frac{2}{9}\left(\mu'_{x_3}\right)_1 + \frac{4}{9}\left(\mu'_{x_3}\right)_2 + \frac{4}{9}\left(\mu'_{x_3}\right)_3 + \frac{4}{9}\left(\mu'_{x_3}\right)_4 + \frac{4}{9}\left(\mu'_{x_3}\right)_5 \\
D_{2000} &= \frac{4}{9\sqrt{5}}\left(\mu'_{x_3}\right)_1 - \frac{4}{9\sqrt{5}}\left(\mu'_{x_3}\right)_2 + \frac{8}{9\sqrt{5}}\left(\mu'_{x_3}\right)_3 - \frac{4}{9\sqrt{5}}\left(\mu'_{x_3}\right)_4 - \frac{4}{9\sqrt{5}}\left(\mu'_{x_3}\right)_5 \\
D_{0020} &= \frac{4}{9\sqrt{5}}\left(\mu'_{x_3}\right)_1 - \frac{4}{9\sqrt{5}}\left(\mu'_{x_3}\right)_2 - \frac{4}{9\sqrt{5}}\left(\mu'_{x_3}\right)_3 + \frac{8}{9\sqrt{5}}\left(\mu'_{x_3}\right)_4 - \frac{4}{9\sqrt{5}}\left(\mu'_{x_3}\right)_5 \\
D_{2020} &= \frac{8}{45}\left(\mu'_{x_3}\right)_1 + \frac{4}{45}\left(\mu'_{x_3}\right)_2 - \frac{8}{45}\left(\mu'_{x_3}\right)_3 - \frac{8}{45}\left(\mu'_{x_3}\right)_4 + \frac{4}{45}\left(\mu'_{x_3}\right)_5 \\
D_{2-222} &= \frac{4}{15}\left(\mu'_{x_3}\right)_2 - \frac{4}{15}\left(\mu'_{x_3}\right)_5
\end{aligned}\right\} \tag{35}$$

In calculating pressure-induced translational or rotational absorption with any model, or pressure-induced vibrational absorption with anharmonicity and H_2 vibration-rotation interaction, μ_{x_3} is also expanded in spherical harmonics

$$\mu_{x_3} = \sum_{l_1=0}^{\infty} \sum_{\mu_1=-l_1}^{l_1} \sum_{l_2=0}^{\infty} \sum_{\mu_2=-l_2}^{l_2} 2\pi C_{l_1\mu_1 l_2\mu_2}(R) Y_{l_1\mu_1}(\theta_1, \varphi_1) Y_{l_2\mu_2}(\theta_2, \varphi_2) \tag{36}$$

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, μ_{x_3} is zero for configurations 1, 2, and 5 and

$$\left(\mu_{x_3}\right)_3 = -\left(\mu_{x_3}\right)_4 \tag{37}$$

Combining equations (33), (36), and (37), using table II, and invoking the equality of C_{2-222} and C_{222-2} gave

$$\left.\begin{aligned}
0 &= \frac{1}{2} C_{0000} + \sqrt{\frac{5}{4}} C_{2000} + \sqrt{\frac{5}{4}} C_{0020} + \frac{5}{2} C_{2020} \\
0 &= \frac{1}{2} C_{0000} - \sqrt{\frac{5}{16}} C_{2000} - \sqrt{\frac{5}{16}} C_{0020} + \frac{5}{8} C_{2020} + \frac{15}{8} C_{2-222} \\
\left(\mu_{x_3}\right)_3 &= \frac{1}{2} C_{0000} + \sqrt{\frac{5}{4}} C_{2000} - \sqrt{\frac{5}{16}} C_{0020} - \frac{5}{4} C_{2020} \\
-\left(\mu_{x_3}\right)_3 &= \frac{1}{2} C_{0000} - \sqrt{\frac{5}{16}} C_{2000} + \sqrt{\frac{5}{4}} C_{0020} - \frac{5}{4} C_{2020} \\
0 &= \frac{1}{2} C_{0000} - \sqrt{\frac{5}{16}} C_{2000} - \sqrt{\frac{5}{16}} C_{0020} + \frac{5}{8} C_{2020} - \frac{15}{8} C_{2-222}
\end{aligned}\right\} \tag{38}$$

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

$$C_{2000} = \frac{4}{3\sqrt{5}} \left(\mu_{x_3}\right)_3 = -C_{0020} \tag{39}$$

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

$$\mu_{x_3} = \mu_{ax_3} + \mu_{qx_3} \tag{40}$$

$$\mu'_{x_3} = \mu'_{ax_3} + \mu'_{qx_3} \tag{41}$$

$$C_{l_1\mu_1 l_2\mu_2} = C_{al_1\mu_1 l_2\mu_2} + C_{ql_1\mu_1 l_2\mu_2} \tag{42}$$

$$D_{l_1\mu_1 l_2\mu_2} = D_{al_1\mu_1 l_2\mu_2} + D_{ql_1\mu_1 l_2\mu_2} \tag{43}$$

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 H_2 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 μ_{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 $\Theta_{l\mu}$)

$$
\left.
\begin{aligned}
C_{q0000} &= 0 & C_{q2-121} &= \frac{2}{5R^4}(Q_{ab}\Delta_{cd} - Q_{cd}\Delta_{ab}) \\
C_{q2000} &= \frac{6\sqrt{5}}{5}\frac{Q_{ab}\alpha_{cd}}{R^4} & C_{q212-1} &= \frac{2}{5R^4}(Q_{ab}\Delta_{cd} - Q_{cd}\Delta_{ab}) \\
C_{q0020} &= -\frac{6\sqrt{5}}{5}\frac{Q_{cd}\alpha_{ab}}{R^4} & C_{q2-222} &= 0 \\
C_{q2020} &= \frac{4}{5R^4}(Q_{ab}\Delta_{cd} - Q_{cd}\Delta_{ab}) & C_{q222-2} &= 0
\end{aligned}
\right\} \tag{44}
$$

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

$$
Q_{ab} = -Q_{XX} = -Q_{YY} = \frac{1}{2} Q_{ZZ} \tag{45}
$$

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 $\overline{ab}$. The quantities Q_{XX}, Q_{YY}, and Q_{ZZ} are elements of the quadrupole moment tensor of molecule a-b. The quantities α_{ab} and Δ_{ab} are the average polarizability and anisotropy of the polarizability, respectively, of molecule a-b. Equations (44) may all be written

$$C_{ql_1\mu_1l_2\mu_2} = \frac{c_{l_1\mu_1l_2\mu_2}}{R^4} \tag{46}$$

where each $c_{l_1\mu_1l_2\mu_2}$ 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

$$\left.\begin{aligned}
D_{q0000} &= 0 & D_{q2-121} &= \frac{2}{5}\,\frac{Q'\Delta - Q\Delta'}{R^4} \\
D_{q2000} &= \frac{6\sqrt{5}}{5}\,\frac{Q'\alpha}{R^4} & D_{q212-1} &= \frac{2}{5}\,\frac{Q'\Delta - Q\Delta'}{R^4} \\
D_{q0020} &= -\frac{6\sqrt{5}}{5}\,\frac{Q\alpha'}{R^4} & D_{q2-222} &= 0 \\
D_{q2020} &= \frac{4}{5}\,\frac{Q'\Delta - Q\Delta'}{R^4} & D_{q222-2} &= 0
\end{aligned}\right\} \tag{47}$$

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

$$D_{ql_1\mu_1l_2\mu_2} = \frac{d_{l_1\mu_1l_2\mu_2}}{R^4} \tag{48}$$

where each $d_{l_1\mu_1l_2\mu_2}$ 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

Internuclear distance, r		Orbital exponent of both atoms, $\bar{\zeta}$			
		1.087 bohr^{-1}	2.054×10^{10} m^{-1}	1.174 bohr^{-1}	2.219×10^{10} m^{-1}
		Repulsive distortion parameter, λ			
		Used in H_2-H calculations		Used in H_2-H_2 calculations	
bohr	m	bohr^{-1}	m^{-1}	bohr^{-1}	m^{-1}
2.5	0.1323×10^{-9}	-0.8179×10^{-1}	-0.1546×10^{10}	-0.9688×10^{-1}	-0.1831×10^{10}
3.0	.1588	-.4760	$-.8995\times10^{9}$	-.5639	-.1066
3.5	.1852	-.2716	-.5133	-.3170	$-.5991\times10^{9}$
4.0	.2117	-.1509	-.2852	-.1710	-.3231
4.5	.2381	$-.8114\times10^{-2}$	-.1533	$-.8819\times10^{-2}$	-.1667
5.0	.2646	-.4217	$-.7969\times10^{8}$	-.4352	$-.8224\times10^{8}$
5.5	.2910	-.2120	-.4006	-.2063	-.3899
6.0	.3175	-.1034	-.1954	$-.9440\times10^{-3}$	-.1784
6.5	.3440	$-.4905\times10^{-3}$	$-.9269\times10^{7}$	-.4190	$-.7918\times10^{7}$
7.0	.3704	-.2273	-.4295	-.1812	-.3424
7.5	.3969	-.1032	-.1950	$-.7668\times10^{-4}$	-.1449
8.0	.4233	$-.4602\times10^{-4}$	$-.8697\times10^{6}$	-.3181	$-.6011\times10^{6}$
8.5	.4498	-.2020	-.3817	-.1298	-.2453
9.0	.4763	$-.8747\times10^{-5}$	-.1653	$-.5206\times10^{-5}$	$-.9838\times10^{5}$
9.5	.5027	-.3744	$-.7075\times10^{5}$	-.2074	-.3919

Overlap contributions to μ_{x_3} and μ'_{x_3}. - 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 κ and ζ 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 κ' and ζ' 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

Intermolecular distance, R		Expansion coefficient for overlap dipole moment, ${}^{a}C_{a2000}$		Expansion coefficients for derivative of overlap dipole moment									
				D_{a0000}		D_{a2000}		D_{a0020}		D_{a2020}		D_{a2-222} and D_{a222-2}	
bohr	m	au	C m	au	C	au	C	au	C	au	C	au	C
4.0	0.2117×10^{-9}	-0.5942×10^{-3}	-0.5038×10^{-32}	0.1450	0.2323×10^{-19}	0.0120	0.0192×10^{-19}	0.0146	0.0234×10^{-19}	0.0015	0.0024×10^{-19}	0.0002	0.0003×10^{-19}
4.2	.2223	-.4791	-.4062	.1139	.1825	.0096	.0154	.0119	.0191	.0012	.0019	.0001	.0002
4.4	.2328	-.3768	-.3194	$.8895\times10^{-1}$	.1425	$.0767\times10^{-1}$	.0123	$.0970\times10^{-1}$	.0155	$.0099\times10^{-1}$	.0016	$.0009\times10^{-1}$	.0001
4.6	.2434	-.2928	-.2482	.6896	.1105	.0611	.0098	.0783	.0125	.0080	.0013	.0006	.0001
4.8	.2540	-.2255	-.1912	.5310	$.8507\times10^{-20}$	.0484	$.0775\times10^{-20}$	.0628	$.1006\times10^{-20}$	.0066	$.0106\times10^{-20}$	.0004	$.0007\times10^{-20}$
5.0	.2646	-.1729	-.1466	.4060	.6505	.0380	.0609	.0499	.0799	.0054	.0087	.0003	.0005
5.2	.2752	-.1323	-.1122	.3083	.4939	.0296	.0474	.0394	.0631	.0044	.0070	.0002	.0004
5.4	.2858	-.1013	$-.8588\times10^{-33}$	.2325	.3725	.0229	.0367	.0308	.0493	.0036	.0058	.0002	.0002
5.6	.2963	$-.7738\times10^{-4}$	-.6560	.1742	.2791	.0175	.0280	.0239	.0383	.0029	.0046	.0001	.0002
5.8	.3069	-.5900	-.5002	.1298	.2080	.0133	.0213	.0184	.0295	.0023	.0037	.0001	.0001
6.0	.3175	-.4505	-.3819	$.9608\times10^{-2}$	.1539	$.0997\times10^{-2}$	.0160	$.1404\times10^{-2}$	.0225	$.0184\times10^{-2}$	.0029	$.0005\times10^{-2}$	.0001
6.2	.3281	-.3421	-.2900	.7075	.1133	.0743	.0119	.1064	.0170	.0144	.0023	.0003	.0001
6.4	.3387	-.2589	-.2195	.5182	$.8302\times10^{-21}$	.0550	$.0881\times10^{-21}$	.0800	$.1282\times10^{-21}$	.0112	$.0179\times10^{-21}$	.0002	$.0004\times10^{-21}$
6.6	.3493	-.1956	-.1658	.3776	.6050	.0403	.0646	.0598	.0958	.0087	.0139	.0001	.0002
6.8	.3598	-.1467	-.1244	.2739	.4388	.0293	.0469	.0444	.0711	.0066	.0106	.0001	.0002
7.0	.3704	-.1097	$-.9300\times10^{-34}$	.1978	.3169	.0212	.0340	.0327	.0524	.0050	.0080	.0001	.0001
7.2	.3810	$-.8143\times10^{-5}$	-.6903	.1422	.2278	.0152	.0244	.0240	.0385	.0037	.0059	.0000	.0001
7.4	.3916	-.6013	-.5098	.1019	.1633	.0109	.0175	.0175	.0280	.0028	.0045	.0000	.0000
7.6	.4022	-.4426	-.3752	$.7273\times10^{-3}$	.1165	$.0774\times10^{-3}$	.0124	$.1271\times10^{-3}$	.0204	$.0207\times10^{-3}$	.0033	$.0002\times10^{-3}$	.0000
7.8	.4128	-.3226	-.2735	.5172	$.8286\times10^{-22}$	.0547	$.0876\times10^{-22}$	.0918	$.1471\times10^{-22}$	.0152	$.0244\times10^{-22}$	.0001	$.0002\times10^{-22}$
8.0	.4233	-.2347	-.1990	.3666	.5873	.0384	.0615	.0661	.1059	.0111	.0178	.0001	.0001

${}^{a}C_{a0020} = -C_{a2000}$

-0.037 bohr^{-2} (-0.132×10^{20} m^{-2}) and -0.247 bohr^{-2} (-0.882×10^{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 (2.117×10^{-10} to 4.233×10^{-10} m). The expansion coefficients are tabulated in table IV.

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

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

TABLE V. - EXPANSION COEFFICIENTS FOR QUADRUPOLE-INDUCED CONTRIBUTION TO COMPONENTS OF DIPOLE MOMENT AND THEIR DERIVATIVES

Collision	Coefficient for quadrupole-induced contribution to component of dipole moment			Coefficient for quadrupole-induced contribution to derivative of component of dipole moment		
	Coefficient	Value of coefficient		Coefficient	Value of coefficient	
		au	C m^5		au	C m^4
H_2-H_2	c_{2000}	6.3749	0.42377×10^{-69}	d_{0000}	0	0
	c_{0020}	-6.3749	-.42377	d_{2000}	7.393	.9287×10^{-59}
				d_{0020}	-5.350	-.6721
				d_{2020}	-.4713	-.5920×10^{-60}
				d_{2-222}	0	0
				d_{222-2}	0	0
H_2-H	c_{00}	0	0	d_{00}	0	0
	c_{20}	3.9124	.26007×10^{-69}	d_{20}	4.537	.5699×10^{-59}
	c_{40}	0	0	d_{40}	0	0
	g_{21}	-2.2588	-.15015×10^{-69}	h_{21}	-2.620	-.3291×10^{-59}

TABLE VI. - COEFFICIENTS FOR QUADRUPOLE-INDUCED CONTRIBUTION TO COMPONENTS OF DIPOLE MOMENT AND THEIR DERIVATIVES FOR VARIOUS CONFIGURATIONS

Collision	Configuration	Component	Coefficient for quadrupole-induced contribution to component of dipole moment[a]		Coefficient for quadrupole-induced contribution to derivative of component of dipole moment[a]	
			au	C m^5	au	C m^4
H_2-H_2	1	x_3	0	0	1.108	0.0139×10^{-58}
	2	↓	0	0	-1.438	-.0181
	3		10.691	$.71067\times10^{-69}$	11.846	.1488
	4		-10.691	-.71067	-9.524	-.1196
	5		0	0	-1.438	-.0181
H_2-H	1	x_1	0	0	0	0
	1	x_3	6.1860	$.41121\times10^{-69}$	7.174	$.9012\times10^{-59}$
	2	x_1	-3.0930	-.20560	-3.587	-.4506
	2	x_3	1.5465	.10280	1.793	.2252
	3	x_1	0	0	0	0
	3	x_3	-3.0930	$-.20560\times10^{-69}$	-3.587	$-.4506\times10^{-59}$

[a]Coefficients must be divided by R^4 to obtain the component of the dipole moment or its derivative.

tions 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_{x_3} and μ'_{x_3}. - 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_{x_3} (eq. (40)) and μ'_{x_3} (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 (2.117×10^{-10} and 2.646×10^{-10} m). The disagreement between the present

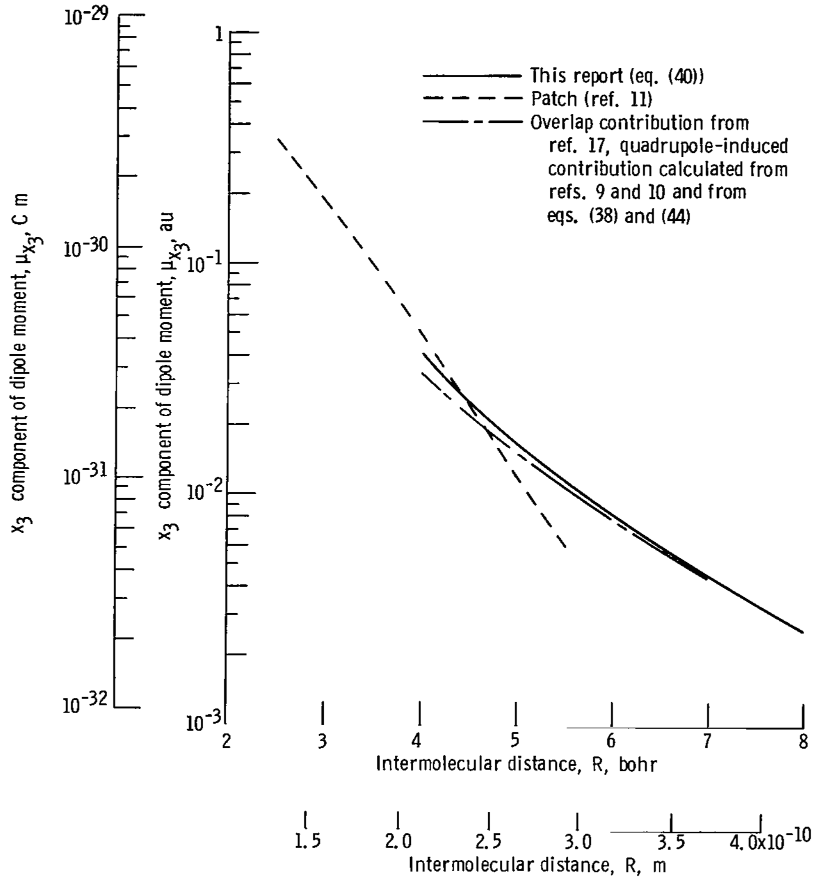
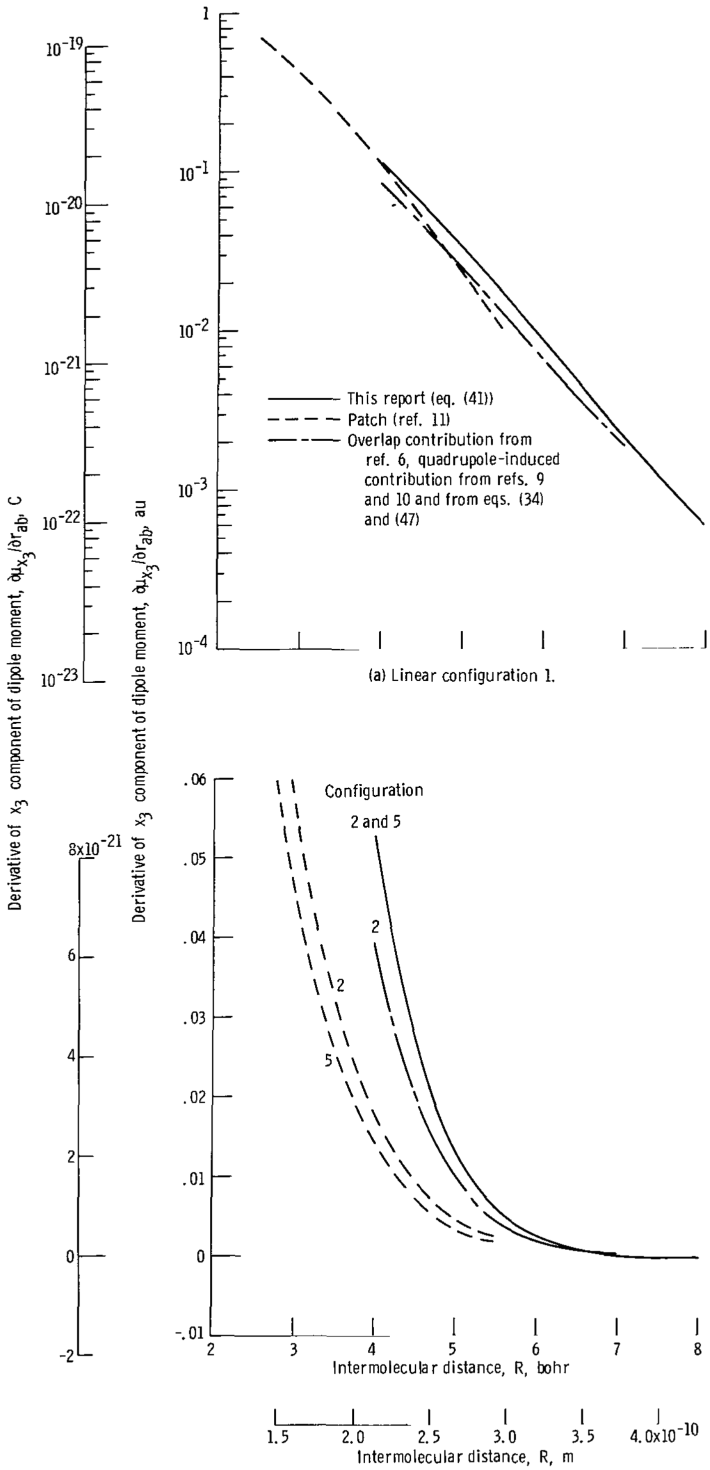
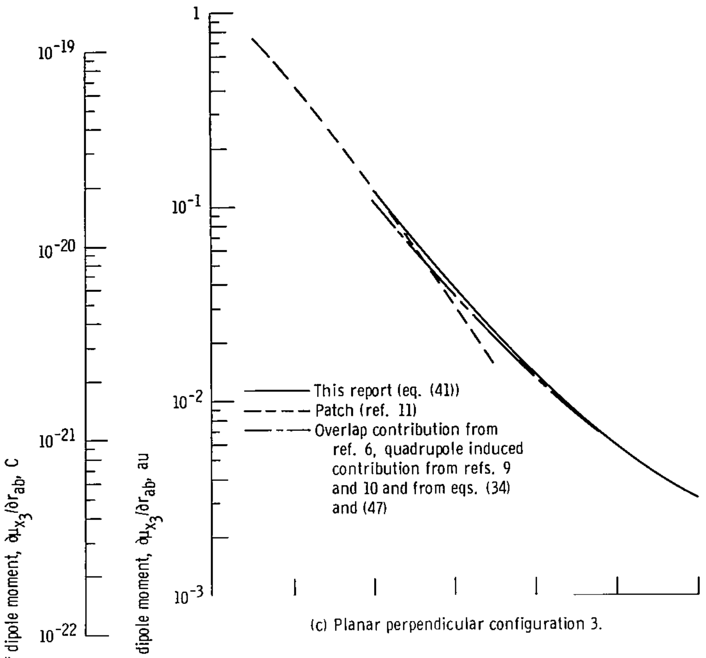


Figure 3. - x_3 component of dipole moment for H_2-H_2 configuration 3. Dipole moment of configuration 4 is the same except for sign. Configurations 1, 2, and 5 have no x_3 component of dipole moment.

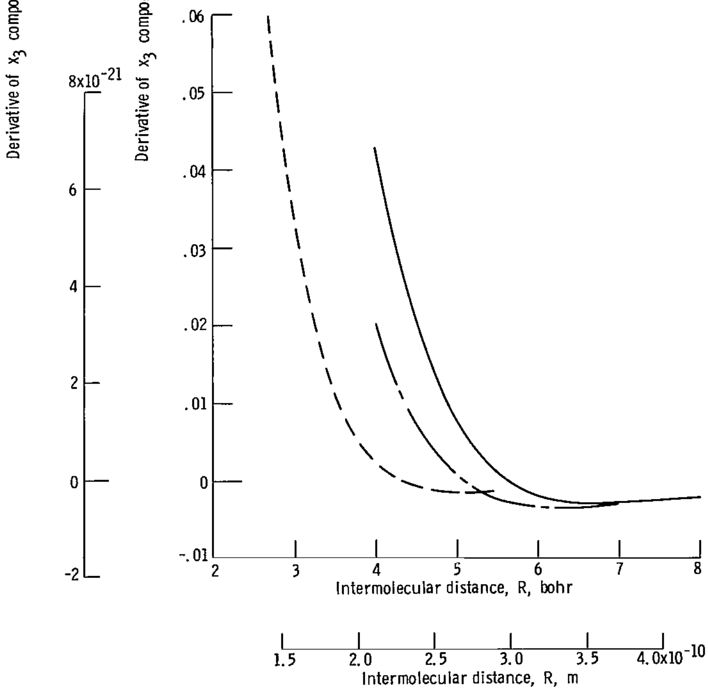


(b) Quadrilateral configuration 2 and nonplanar perpendicular configuration 5. The difference in the derivatives for configuration 2 and 5 according to equation (41) is too small to show.

Figure 4. - Derivative of x_3 component of dipole moment in H_2-H_2 collisions.



(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 overlap 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 μ'_{x_3} in figures 4(b) and (d) are only about one-half those in figures 4(a) and (c), so the lack of agreement between 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 $\bar{\zeta}$ used in calculating λ: 1.000 bohr^{-1} ($1.890\times10^{10}\ \text{m}^{-1}$) in reference 6, and 1.174 bohr^{-1} ($2.219\times10^{10}\ \text{m}^{-1}$) in the present work. The latter value is the same as used for the orbitals in the H_2-H_2 calculation and is thus consistent. Also, it gives better agreement with the measured integrated absorption coefficient of the fundamental 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 H_2-H_2 pressure-induced fundamental vibrational transition was calculated for a temperature of 298 K. The method of calculation was based on reference 6 with the following major changes:

(1) The H_2-H_2 average interaction energy was assumed to be a Morse potential (ref. 19) for R greater than 4 bohr (2.117×10^{-10} m). For R less than 4 bohr, an exponential was fitted to the Morse potential at 4 bohr and an ab initio energy (ref. 11) at 2.5 bohr (1.323×10^{-10} m).

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

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

(4) The quantities μ_{x_3} and μ'_{x_3} from reference 11 were used for R between 2.5 and 4 bohr (1.323×10^{-10} and 2.117×10^{-10} m). The quantities μ_{x_3} and μ'_{x_3} from tables IV and V were used for R between 6 and 8 bohr (3.175×10^{-10} and 4.233×10^{-10} m). Between 4 and 6 bohr the expansion coefficients for μ_{x_3} and μ'_{x_3} were faired into results from reference 11 at R = 4 bohr (2.117×10^{-10} m) and tables IV and V at R = 6 bohr

(3.175×10^{-10} m) by setting each expansion coefficient equal to $f_1R^{-4} + f_2 + f_3R + f_4R^2$, 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 (4.233×10^{-10} 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 H_2-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 H_2-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.

DIPOLE MOMENT AND ITS DERIVATIVE IN H_2-H COLLISIONS

Analysis

Just as for H_2-H_2, the dipole moment of 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 H_2-H_2 except that (1) the repulsive distortion parameter λ is based on a repulsive H-H calculation using an orbital exponent $\bar{\zeta}$ which is the average of the orbital exponents for H and H_2, (2) the x_1 components of $\vec{\mu}$ 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 τ are used in evaluating molecular integrals because of the appreciable difference between 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 θ_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 φ_1 is zero.

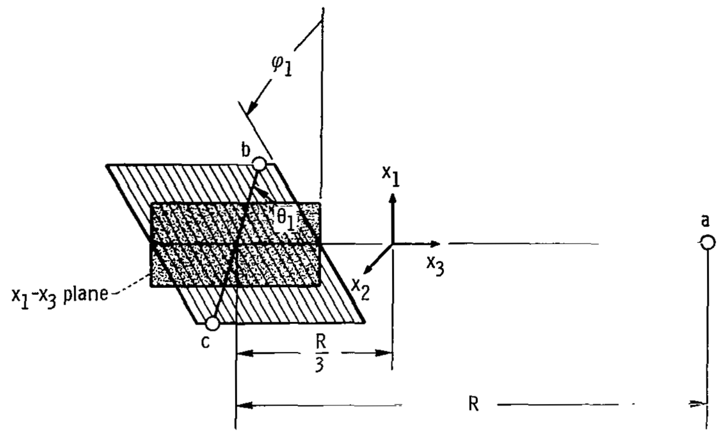


Figure 5. - Coordinates in H_2-H collisions. The molecule is b-c and the atom is is at a; protons are located at a, b, and c; the x_3 axis passes through the centers of the molecule and the atom; θ_1 and φ_1 are polar and azimuthal angles, respectively.

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)

$$\Psi = \psi_1 - \psi_2 \tag{49}$$

where the determinantal wave functions ψ_1 and ψ_2 are given by

$$\left.\begin{aligned}\psi_1 &\equiv (3!)^{-1/2}\det\left[a(1)\alpha(1), b(2)\beta(2), c(3)\alpha(3)\right]\\ \psi_2 &\equiv (3!)^{-1/2}\det\left[a(1)\alpha(1), b(2)\alpha(2), c(3)\beta(3)\right]\end{aligned}\right\} \tag{50}$$

The x_j component of $\vec{\mu}_a$ is given by

$$\mu_{ax_j} = \frac{-\int \Psi^2 \sum_{i=1}^{3} x_{ji}\, dV_1\, dV_2\, dV_3}{\int \Psi^2\, dV_1\, dV_2\, dV_3} \qquad (j = 1, 3) \tag{51}$$

If equation (10) is assumed to hold, and integrals are defined as in equations (5) to (9) except for generalizing the subscript 3 to j, equation (51) becomes

$$\mu_{ax_j} = \frac{N_{x_j}}{E} \qquad (j = 1, 3) \tag{52}$$

where

$$N_{x_j} \equiv -2\left(m_{jaa} + m_{jbb} + m_{jcc} + m_{jaa}S_{bc}^2 + 2m_{jbc}S_{bc}\right) + 2\left(m_{jac}s_{ac} + m_{jab}s_{ab} + m_{jab}S_{bc}s_{ac} + m_{jac}S_{bc}s_{ab}\right) + m_{jbb}s_{ac}^2 + m_{jcc}s_{ab}^2 + 2m_{jbc}s_{ab}s_{ac} \qquad (j = 1, 3) \tag{53}$$

$$E \equiv 2 + 2S_{bc}^2 - s_{ac}^2 - s_{ab}^2 - 2S_{bc}s_{ab}s_{ac} \tag{54}$$

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

$$\left.\begin{aligned}
a(i) &= \left(\frac{\zeta_a^3}{\pi}\right)^{1/2} e^{-\zeta_a r_{ai}}\left(1 + \lambda_{ab} r_{ai} \cos \theta_{abi} + \lambda_{ac} r_{ai} \cos \theta_{aci}\right) \\
b(i) &= \left(\frac{\zeta_{bc}^3}{\pi}\right)^{1/2} e^{-\zeta_{bc} r_{bi}}\left(1 + \kappa r_{bi} \cos \theta_{bci} + \lambda_{ab} r_{bi} \cos \theta_{bai}\right) \\
c(i) &= \left(\frac{\zeta_{bc}^3}{\pi}\right)^{1/2} e^{-\zeta_{bc} r_{ci}}\left(1 + \kappa r_{ci} \cos \theta_{cbi} + \lambda_{ac} r_{ci} \cos \theta_{cai}\right)
\end{aligned}\right\} (i = 1, 2, 3) \tag{55}$$

where ζ_a is the orbital exponent for the atom (1 bohr^{-1} or $1.890\times10^{10}\ \mathrm{m}^{-1}$) and κ 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 ζ_{bc} and ζ_a, respectively, integrals of type s_{ac} were derived without truncated series expansions in powers of τ_{ac}, where

$$\tau_{ac} \equiv \frac{1}{2} r_{ac}(\zeta_a - \zeta_{bc}) \tag{56}$$

The result is

$$s_{ac} = \frac{1}{2}\left(\zeta_a \zeta_{bc}\right)^{3/2} r_{ac}^3 e^{-\sigma_{ac}}\left\{2M(\sigma_{ac}, \tau_{ac}) + r_{ac}\kappa \cos\theta_{cba}\left[M(\sigma_{ac}, \tau_{ac}) + L(\sigma_{ac}, \tau_{ac})\right]\right\} \tag{57}$$

where

$$\sigma_{ac} \equiv \frac{1}{2} r_{ac}(\zeta_a + \zeta_{bc}) \tag{58}$$

$$M(\sigma, \tau) \equiv \frac{1}{4}\left[A_1(\tau)J_3(\sigma) - A_3(\tau)J_1(\sigma)\right] \tag{59}$$

$$L(\sigma, \tau) \equiv \frac{1}{4}\left[A_4(\tau)J_2(\sigma) - A_2(\tau)J_4(\sigma)\right] \tag{60}$$

$$A_n(\tau) \equiv -e^{-\tau}\left[\frac{1}{\tau} + \frac{n-1}{\tau^2} + \frac{(n-1)(n-2)}{\tau^3} + \ldots + \frac{(n-1)!}{\tau^{n-1}} + \frac{(n-1)!}{\tau^n}\right] - e^{\tau}\left[\frac{(-1)^n}{\tau}\right.$$
$$\left. + \frac{(-1)^{n-1}(n-1)}{\tau^2} + \frac{(-1)^{n-2}(n-1)(n-2)}{\tau^3} + \ldots + \frac{(n-1)!}{\tau^{n-1}} - \frac{(n-1)!}{\tau^n}\right] \tag{61}$$

$$J_n(\sigma) \equiv \frac{(n-1)!}{\sigma^n}\left[1 + \sigma + \frac{\sigma^2}{2!} + \ldots + \frac{\sigma^{n-1}}{(n-1)!}\right] \tag{62}$$

Integrals of type m_{jaa} were treated in a fashion similar to m_{3aa} for H_2-H_2, with the result

$$m_{jaa} = \frac{2}{\zeta_a^2}\left(\lambda_{ab}\cos\theta_{abx_j} + \lambda_{ac}\cos\theta_{acx_j}\right) \qquad (j = 1, 3) \tag{63}$$

$$m_{jbb} = \frac{2}{\zeta_{bc}^2}\left(\kappa\cos\theta_{bcx_j} - \lambda_{ab}\cos\theta_{abx_j}\right) \qquad (j = 1, 3) \tag{64}$$

The integral m_{jcc} is similar to m_{jbb}.

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

$$m_{jbc} = \frac{1}{4}\zeta_{bc}^{3} r_{bc}^{5} e^{-\sigma_{bc}}\left\{\lambda_{ab}\left[\cos\theta_{bca}\cos\theta_{bcx_j}U(\sigma_{bc}) + \sin\theta_{bca}\sin\theta_{bcx_j}\cos\varphi_{abcx_j}T(\sigma_{bc})\right] + \lambda_{ac}\left[-\cos\theta_{cba}\cos\theta_{bcx_j}U(\sigma_{bc}) + \sin\theta_{cba}\sin\theta_{bcx_j}\cos\varphi_{abcx_j}T(\sigma_{bc})\right]\right\} \quad (j = 1, 3) \tag{65}$$

where σ_{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 τ_{ac}

$$m_{jac} = \frac{1}{4}\left(\zeta_a\zeta_{bc}\right)^{3/2} r_{ac}^{5} e^{-\sigma_{ac}}\left(-2\cos\theta_{acx_j}L(\sigma_{ac},\tau_{ac})\left(\frac{1}{r_{ac}} + \lambda_{ac}\right) + \kappa\left\{\cos\theta_{cba}\cos\theta_{acx_j}\left[-U(\sigma_{ac},\tau_{ac}) - L(\sigma_{ac},\tau_{ac})\right] + \sin\theta_{cba}\sin\theta_{acx_j}\cos\varphi_{bacx_j}T(\sigma_{ac},\tau_{ac})\right\} + \lambda_{ab}\left\{\cos\theta_{abc}\cos\theta_{acx_j}\left[U(\sigma_{ac},\tau_{ac}) - L(\sigma_{ac},\tau_{ac})\right] + \sin\theta_{abc}\sin\theta_{acx_j}\cos\varphi_{bacx_j}T(\sigma_{ac},\tau_{ac})\right\}\right) \quad (j = 1, 3) \tag{66}$$

where

$$T(\sigma,\tau) \equiv \frac{1}{8}\left\{J_5(\sigma)\left[A_1(\tau) - A_3(\tau)\right] + J_3(\sigma)\left[A_5(\tau) - A_1(\tau)\right] + J_1(\sigma)\left[A_3(\tau) - A_5(\tau)\right]\right\} \tag{67}$$

$$U(\sigma, \tau) \equiv \frac{1}{4}\left[J_5(\sigma)A_3(\tau) - J_3(\sigma)A_5(\tau)\right] \qquad (68)$$

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

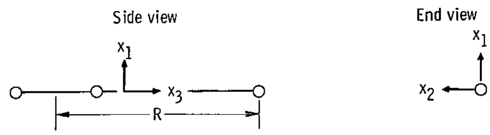
Overlap contribution to derivative of dipole moment. - In calculating the pressure-induced vibrational absorption, the partial derivative of $\vec{\mu}$ with respect to the internuclear distance r_{bc} is necessary. If we let a prime indicate $\partial/\partial r_{bc}$, from equation (52)

$$\mu'_{ax_j} = \frac{N'_{x_j}}{E} - \frac{N_{x_j}E'}{E^2} \qquad (j = 1, 3) \qquad (69)$$

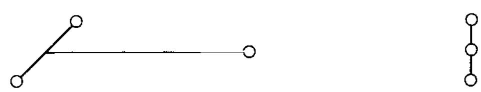
where N'_{x_j} and E' were found by differentiating equations (53), (54), (57), (63) to (66), etc., analytically.

Configurations and expansion coefficients. - In calculating the pressure-induced vibrational absorption for H_2 colliding with an atom (ref. 21), μ'_{x_3} is expanded in normalized Legendre polynomials $\Theta_{l0}(\theta)$

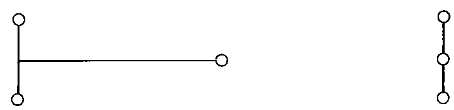
$$\mu'_{x_3} = \sum_{l=0}^{\infty} D_{l0}(R)\Theta_{l0}(\theta_1) \qquad (70)$$



(a) Linear configuration 1.



(b) Scalene configuration 2. The molecule is at 45° to the intermolecular axis (x_3 axis).



(c) Isosceles configuration 3.

Figure 6. - Configurations used in calculations for H_2-H collisions. Intermolecular distance R had values from 4 to 8 bohr (2.117×10^{-10} to 4.233×10^{-10} m). The molecule had an internuclear distance of 1.401446 bohr (0.741599×10^{-10} m).

The fact that molecule b-c is homonuclear requires that Θ_{l0} be zero when l 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

$$\left.\begin{aligned}
\left(\mu'_{x_3}\right)_1 &= \frac{1}{\sqrt{2}} D_{00} + \frac{\sqrt{10}}{2} D_{20} + \frac{3\sqrt{2}}{2} D_{40} \\
\left(\mu'_{x_3}\right)_2 &= \frac{1}{\sqrt{2}} D_{00} + \frac{\sqrt{10}}{8} D_{20} - \frac{39\sqrt{2}}{64} D_{40} \\
\left(\mu'_{x_3}\right)_3 &= \frac{1}{\sqrt{2}} D_{00} - \frac{\sqrt{10}}{4} D_{20} + \frac{9\sqrt{2}}{16} D_{40}
\end{aligned}\right\} \tag{71}$$

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

$$\left.\begin{aligned}
D_{00} &= \frac{\sqrt{2}}{15}\left(\mu'_{x_3}\right)_1 + \frac{8\sqrt{2}}{15}\left(\mu'_{x_3}\right)_2 + \frac{2\sqrt{2}}{5}\left(\mu'_{x_3}\right)_3 \\
D_{20} &= \frac{20}{21\sqrt{10}}\left(\mu'_{x_3}\right)_1 + \frac{16}{21\sqrt{10}}\left(\mu'_{x_3}\right)_2 - \frac{12}{7\sqrt{10}}\left(\mu'_{x_3}\right)_3 \\
D_{40} &= \frac{32}{105\sqrt{2}}\left(\mu'_{x_3}\right)_1 - \frac{64}{105\sqrt{2}}\left(\mu'_{x_3}\right)_2 + \frac{32}{105\sqrt{2}}\left(\mu'_{x_3}\right)_3
\end{aligned}\right\} \tag{72}$$

In calculating absorption coefficients it is convenient to take linear combinations of μ_{x_1} and μ_{x_2}. For any configuration

$$\left.\begin{aligned}
\mu_{(1)} &\equiv (2)^{-1/2}\left(\mu_{x_1} + i\mu_{x_2}\right), \quad \mu_{(-1)} \equiv (2)^{-1/2}\left(\mu_{x_1} - i\mu_{x_2}\right) \\
\mu'_{(1)} &\equiv (2)^{-1/2}\left(\mu'_{x_1} + i\mu'_{x_2}\right), \quad \mu'_{(-1)} \equiv (2)^{-1/2}\left(\mu'_{x_1} - i\mu'_{x_2}\right)
\end{aligned}\right\} \tag{73}$$

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

$$\mu'_{(1)} = \sum_{l=0}^{\infty} \sum_{\mu=-l}^{l} \sqrt{2\pi}\, H_{l\mu}(R) Y_{l\mu}(\theta_1, \varphi_1) \tag{74}$$

Because of the symmetry and the three configurations considered, all of which have φ_1, μ_{x_2}, and μ'_{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

$$H_{21} = \frac{4}{\sqrt{15}} \left(\mu'_{(1)}\right)_2 = \frac{4}{\sqrt{30}} \left(\mu'_{x_1}\right)_2 \tag{75}$$

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

$$\mu_{x_3} = \sum_{l=0}^{\infty} C_{l0}(R) \Theta_{l0}(\theta_1) \tag{76}$$

which gave

$$\left.\begin{aligned}
C_{00} &= \frac{\sqrt{2}}{15} \left(\mu_{x_3}\right)_1 + \frac{8\sqrt{2}}{15} \left(\mu_{x_3}\right)_2 + \frac{2\sqrt{2}}{5} \left(\mu_{x_3}\right)_3 \\
C_{20} &= \frac{20}{21\sqrt{10}} \left(\mu_{x_3}\right)_1 + \frac{16}{21\sqrt{10}} \left(\mu_{x_3}\right)_2 - \frac{12}{7\sqrt{10}} \left(\mu_{x_3}\right)_3 \\
C_{40} &= \frac{32}{105\sqrt{2}} \left(\mu_{x_3}\right)_1 - \frac{64}{105\sqrt{2}} \left(\mu_{x_3}\right)_2 + \frac{32}{105\sqrt{2}} \left(\mu_{x_3}\right)_3
\end{aligned}\right\} \tag{77}$$

Also, $\mu_{(1)}$ was expanded

$$\mu_{(1)} = \sum_{l=0}^{\infty} \sum_{\mu=-l}^{l} \sqrt{2\pi}\, G_{l\mu}(R) Y_{l\mu}(\theta_1, \varphi_1) \tag{78}$$

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

$$G_{21} = \frac{4}{\sqrt{15}} \left(\mu_{(1)}\right)_2 = \frac{4}{\sqrt{30}} \left(\mu_{x_1}\right)_2 \tag{79}$$

Although equations (70) to (79) were derived for $\vec{\mu}'$ and $\vec{\mu}$, they are linear and therefore equally applicable to the overlap and quadrupole-induced contributions to the expansion coefficients and components of $\vec{\mu}'$ and $\vec{\mu}$ just as for H_2-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 $\vec{F}$ due to a point quadrupole and the relation $\vec{\mu} = \vec{F}\alpha_a$, where α_a is the polarizability of an H atom. The expansion coefficients are

$$\left.\begin{aligned} C_{q00} &= 0 \\ C_{q20} &= 3\sqrt{\frac{2}{5}}\,\frac{\alpha_a Q}{R^4} \\ C_{q40} &= 0 \\ G_{q21} &= -\sqrt{\frac{6}{5}}\,\frac{\alpha_a Q}{R^4} \end{aligned}\right\} \tag{80}$$

Equations (80) may be written

$$\left.\begin{aligned} C_{ql0} &= \frac{c_{l0}}{R^4} \\ G_{q21} &= \frac{g_{21}}{R^4} \end{aligned}\right\} \tag{81}$$

where each c_{l0} 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)

$$\left.\begin{aligned} D_{q00} &= 0 \\ D_{q20} &= 3\sqrt{\frac{2}{5}}\,\frac{\alpha_a Q'}{R^4} \\ D_{q40} &= 0 \\ H_{q21} &= -\sqrt{\frac{6}{5}}\,\frac{\alpha_a Q'}{R^4} \end{aligned}\right\} \qquad (82)$$

Equations (82) may be written

$$\left.\begin{aligned} D_{ql0} &= \frac{d_{l0}}{R^4} \\ H_{q21} &= \frac{h_{21}}{R^4} \end{aligned}\right\} \qquad (83)$$

where each d_{l0} and h_{21} are constants.

Results and Discussion

Repulsive distortion parameter. - This parameter was calculated just as for H_2-H_2 except that $\overline{\zeta}$ 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 λ are given in table III.

Overlap contributions to μ_{x_i} and μ'_{x_i}. - These contributions were calculated from equations (18) 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 κ, κ', ζ_{bc}, and ζ'_{bc} were the same as used for H_2-H_2, but, of course, ζ_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

Intermolecular distance, R		Expansion coefficients for components of overlap dipole moment							
		C_{a00}		C_{a20}		C_{a40}		G_{a21}	
bohr	m	au	C m	au	C m	au	C m	au	C m
4.0	0.2117×10^{-9}	-0.4086×10^{-1}	-0.3464×10^{-30}	-0.0353×10^{-1}	-0.0299×10^{-30}	-0.0001×10^{-1}	-0.0001×10^{-30}	0.1580×10^{-2}	0.1339×10^{-31}
4.2	.2223	-.3285	-.2785	-.0292	-.0248	-.0001	-.0001	.1186	.1005
4.4	.2328	-.2623	-.2224	-.0239	-.0203	-.0000	-.0000	$.8906\times10^{-3}$	$.7550\times10^{-32}$
4.6	.2434	-.2080	-.1763	-.0195	-.0165	-.0000	-.0000	.6667	.5652
4.8	.2540	-.1639	-.1390	-.0158	-.0134	-.0000	-.0000	.4981	.4223
5.0	.2646	-.1282	-.1087	-.0127	-.0180	-.0000	-.0000	.3708	.3144
5.2	.2752	$-.9972\times10^{-2}$	$-.8454\times10^{-31}$	$-.1007\times10^{-2}$	$-.0854\times10^{-31}$	$-.0002\times10^{-2}$	$-.0002\times10^{-31}$	.2750	.2331
5.4	.2858	-.7707	-.6534	-.0795	-.0674	-.0002	-.0001	.2032	.1723
5.6	.2963	-.5924	-.5022	-.0623	-.0528	-.0001	-.0001	.1495	.1267
5.8	.3069	-.4527	-.3838	-.0484	-.0410	-.0001	-.0001	.1095	$.9283\times10^{-33}$
6.0	.3175	-.3443	-.2919	-.0374	-.0317	-.0001	-.0001	$.7996\times10^{-4}$	.6779
6.2	.3281	-.2606	-.2209	-.0287	-.0243	-.0000	-.0000	.5811	.4926
6.4	.3387	-.1963	-.1664	-.0218	-.0185	-.0000	-.0000	.4204	.3564
6.6	.3493	-.1473	-.1249	-.0165	-.0140	-.0000	-.0000	.3031	.2570
6.8	.3598	-.1100	$-.9326\times10^{-32}$	-.0124	$-.1051\times10^{-32}$	-.0000	$-.0002\times10^{-32}$	.2176	.1845
7.0	.3704	$-.8191\times10^{-3}$	-.6944	$-.0931\times10^{-3}$	-.0789	$-.0001\times10^{-3}$	-.0001	.1557	.1320
7.2	.3810	-.6077	-.5152	-.0693	-.0588	-.0001	-.0000	.1110	$.9410\times10^{-34}$
7.4	.3916	-.4492	-.3808	-.0514	-.0436	-.0000	-.0000	$.7890\times10^{-5}$	.6689
7.6	.4022	-.3311	-.2807	-.0379	-.0321	-.0000	-.0000	.5588	.4737
7.8	.4128	-.2432	-.2062	-.0278	-.0236	-.0000	-.0000	.3941	.3341
8.0	.4233	-.1782	-.1511	-.0204	-.0173	.0000	.0000	.2779	.2356

TABLE VIII. - EXPANSION COEFFICIENTS FOR DERIVATIVES OF COMPONENTS OF OVERLAP DIPOLE MOMENT IN H_2-H COLLISIONS

Intermolecular distance, R		Expansion coefficients for derivatives of components of overlap dipole moment							
		D_{a00}		D_{a20}		D_{a40}		H_{a21}	
bohr	m	au	C	au	C	au	C	au	C
4.0	0.2117×10^{-9}	0.3889×10^{-1}	0.6231×10^{-20}	-0.0157×10^{-1}	-0.0252×10^{-20}	0.0005×10^{-1}	0.0008×10^{-20}	0.1205×10^{-2}	0.1931×10^{-21}
4.2	.2223	.3001	.4808	-.0149	-.0239	.0003	.0005	$.9060\times10^{-3}$	.1452
4.4	.2328	.2299	.3683	-.0136	-.0218	.0002	.0003	.6797	.1089
4.6	.2434	.1748	.2800	-.0121	-.0194	.0001	.0002	.5075	$.8130\times10^{-22}$
4.8	.2540	.1319	.2113	-.0106	-.0170	.0000	.0001	.3772	.6043
5.0	.2646	$.9886\times10^{-2}$	.1584	$-.0908\times10^{-2}$	-.0145	$.0002\times10^{-2}$	.0000	.2790	.4470
5.2	.2752	.7355	.1178	-.0767	-.0123	-.0001	-.0000	.2052	.3288
5.4	.2858	.5433	$.8704\times10^{-21}$	-.0638	$-.1022\times10^{-21}$	-.0002	$-.0002\times10^{-21}$	.1500	.2403
5.6	.2963	.3986	.6386	-.0524	-.0840	-.0002	-.0003	.1090	.1746
5.8	.3069	.2904	.4652	-.0426	-.0682	-.0002	-.0003	$.7868\times10^{-4}$	.1261
6.0	.3175	.2102	.3368	-.0342	-.0548	-.0002	-.0003	.5642	$.9039\times10^{-23}$
6.2	.3281	.1511	.2421	-.0273	-.0437	-.0002	-.0002	.4020	.6440
6.4	.3387	.1079	.1729	-.0215	-.0344	-.0001	-.0002	.2837	.4545
6.6	.3493	$.7657\times10^{-3}$	.1227	$-.1687\times10^{-3}$	-.0270	$-.0010\times10^{-3}$	-.0002	.1990	.3188
6.8	.3598	.5394	$.8642\times10^{-22}$	-.1312	$-.2102\times10^{-22}$	-.0007	$-.0011\times10^{-22}$	.1383	.2216
7.0	.3704	.3776	.6050	-.1013	-.1623	-.0005	-.0009	$.9537\times10^{-5}$	.1528
7.2	.3810	.2625	.4206	-.0777	-.1245	-.0003	-.0005	.6519	.1044
7.4	.3916	.1811	.2901	-.0592	-.0948	-.0002	-.0004	.4403	$.7054\times10^{-24}$
7.6	.4022	.1240	.1987	-.0449	-.0719	-.0001	-.0002	.2943	.4715
7.8	.4128	$.8415\times10^{-4}$	.1348	$-.3386\times10^{-4}$	-.0542	$-.0005\times10^{-4}$	-.0001	.1945	.3116
8.0	.4233	.5662	$.9071\times10^{-23}$	-.2541	$-.4071\times10^{-23}$	-.0002	$-.0002\times10^{-23}$	.1267	.2030

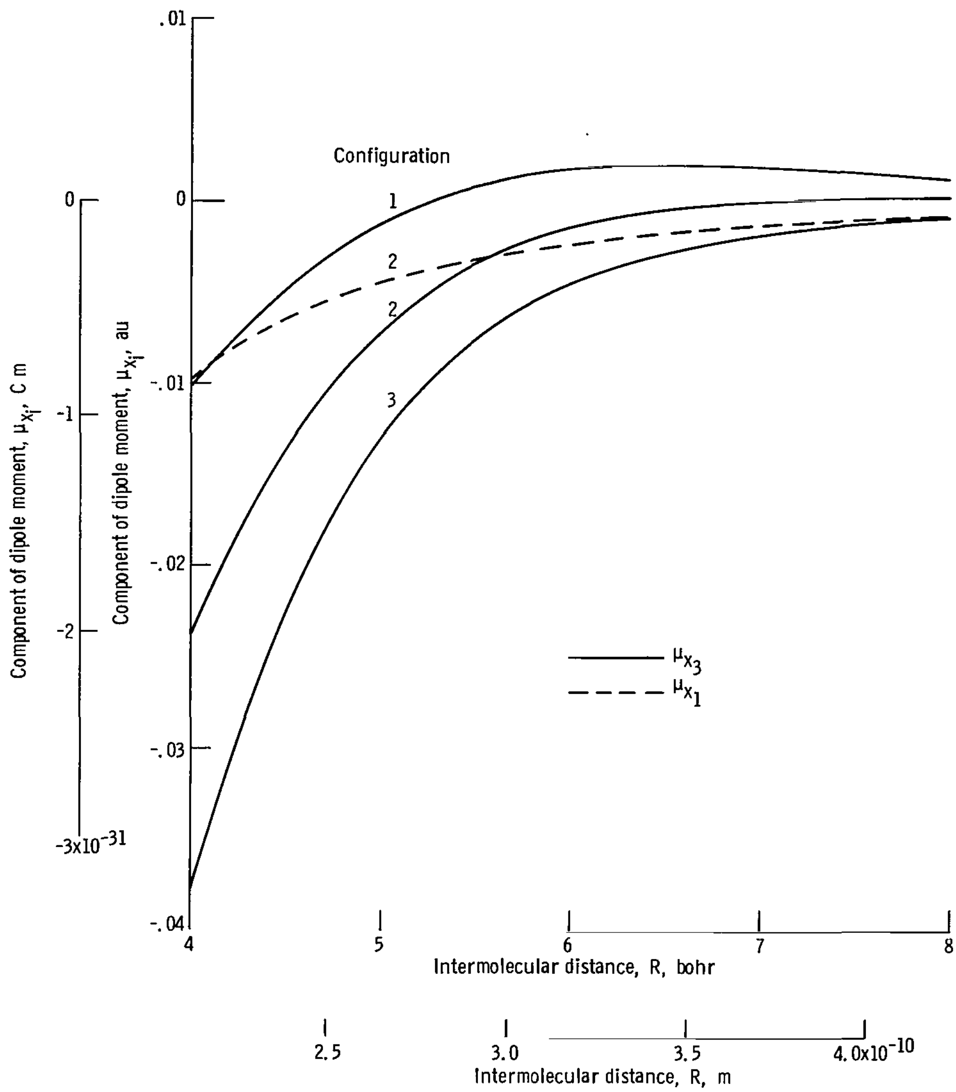


Figure 7. - x_1 and x_3 components of dipole moment in H_2-H collisions. The x_1 component of dipole moment is zero for linear configuration 1 and for isosceles configuration 3. Overlap and quadrupole-induced contributions are included.

intermolecular distances from 4 to 8 bohr (2.117×10^{-10} to 4.233×10^{-10} m). The expansion coefficients are tabulated in tables VII and VIII.

Quadrupole-induced contributions to μ_{x_i} and μ'_{x_i}. - The same values of Q and Q' were used as for H_2-H_2. The polarizability α_a of the H atom was obtained from Pauling and Wilson (ref. 12) and had the value 4.5 au (7.419×10^{-41} C^2 m^2 J^{-1}).

Using these values, the coefficients for the quadrupole-induced contributions to μ_{x_1}, μ_{x_3}, μ'_{x_1}, and μ'_{x_3} were calculated from equations (80) to (83) and are tabulated in table V. The quadrupole-induced contributions to μ_{x_1}, μ_{x_3}, μ'_{x_1}, and μ'_{x_3} 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 μ_{x_1}, μ_{x_3}, μ'_{x_1}, and μ'_{x_3}. - 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.

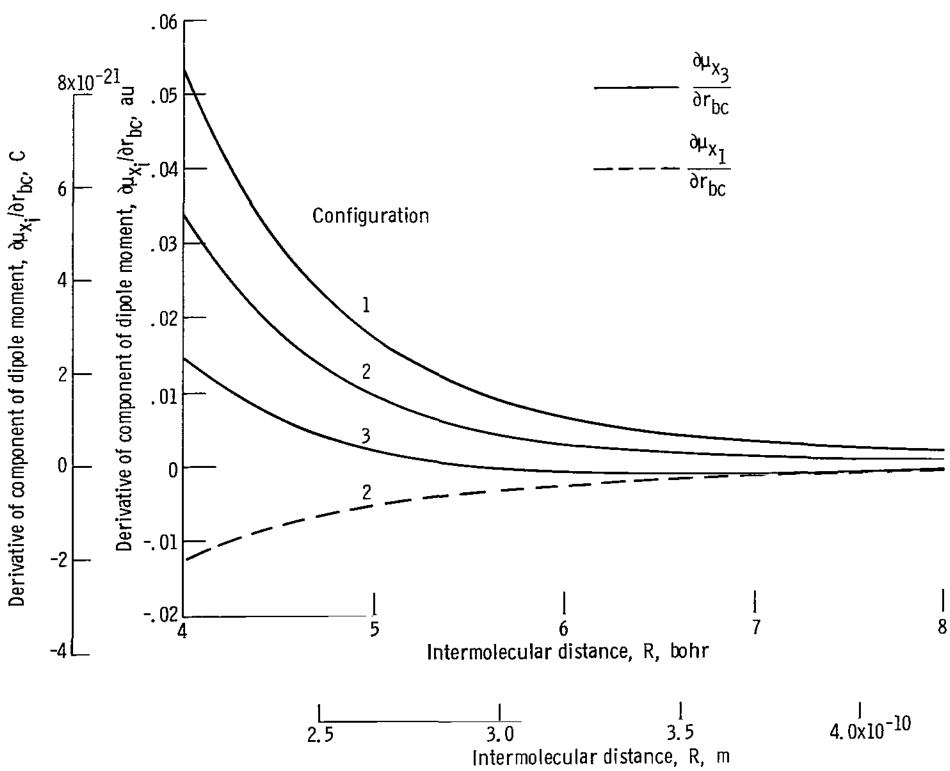


Figure 8. - Derivatives of x_1 and x_3 components of dipole moment in H_2-H collisions. The derivative of the x_1 component of dipole moment is zero for linear configuration 1 and isosceles configuration 3. Overlap and quadrupole-induced contributions are included.

Comparison with other investigations. - For the range of intermolecular distance used, there are no published theoretical or experimental values of $\vec{\mu}$ or $\vec{\mu}'$.

Potential applications. - No application is foreseen until ab initio calculations are made for R less than 4 bohr (2.117×10^{-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 (2.117×10^{-10} to 4.233×10^{-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.

APPENDIX - SYMBOLS

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 τ
$a(i)(i = 1, 2, 3, 4)$	orbital of electron i about proton a, $\mathrm{bohr}^{-3/2}$; $\mathrm{m}^{-3/2}$
$b(i)(i = 1, 2, 3, 4)$	orbital of electron i about proton b, $\mathrm{bohr}^{-3/2}$; $\mathrm{m}^{-3/2}$
$C_{al0}(l = 0, 2, 4)$	expansion coefficient for μ_{ax_3} in H_2-H collision, charge bohr; C m
$C_{al_1\mu_1l_2\mu_2}$	expansion coefficient for μ_{ax_3} in H_2-H_2 collision, charge bohr; C m
$C_{l0}(l = 0, 2, 4)$	expansion coefficient for μ_{x_3} in H_2-H collision, charge bohr; C m
$C_{l_1\mu_1l_2\mu_2}$	expansion coefficient for μ_{x_3} in H_2-H_2 collision, charge bohr; C m
$C_{ql0}(l = 0, 2, 4)$	expansion coefficient for μ_{qx_3} in H_2-H collision, charge bohr; C m
$C_{ql_1\mu_1l_2\mu_2}$	expansion coefficient for μ_{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, $\mathrm{bohr}^{-3/2}$; $\mathrm{m}^{-3/2}$
$c_{l0}(l = 0, 2, 4)$	coefficient for quadrupole-induced contribution to x_3 component of dipole moment in H_2-H collision, charge bohr^5; C m^5
$c_{l_1\mu_1l_2\mu_2}$	coefficient for quadrupole-induced contribution to x_3 component of dipole moment in H_2-H_2 collision, charge bohr^5; C m^5
$D_{al0}(l = 0, 2, 4)$	expansion coefficient for μ'_{ax_3} in H_2-H collision, charge; C
$D_{al_1\mu_1l_2\mu_2}$	expansion coefficient for μ'_{ax_3} in H_2-H_2 collision, charge; C

$D_{l0}(l = 0, 2, 4)$	expansion coefficient for μ'_{x_3} in H_2-H collision, charge; C
$D_{l_1\mu_1 l_2\mu_2}$	expansion coefficient for μ'_{x_3} in H_2-H_2 collision, charge; C
$D_{ql_1\mu_1 l_2\mu_2}$	expansion coefficient for μ'_{qx_3} in H_2-H_2 collision, charge; 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 H_2-H collision, charge $bohr^4$; C m^4
$d_{l_1\mu_1 l_2\mu_2}$	coefficient for quadrupole-induced contribution to x_3 component of derivative of dipole moment in H_2-H_2 collision, charge $bohr^4$; C m^4
dV_i(i = 1, 2, 3, 4)	element of volume for electron i in configuration space and spin space, $bohr^3$; m^3
dv_1	element of volume for electron 1 in configuration space, $bohr^3$; m^3
E	denominator of expression for component of dipole moment
$\vec{F}$	electric field strength vector, hartree $bohr^{-1}$ $charge^{-1}$; J m^{-1} C^{-1}
f_i(i = 1, 2, 3, 4)	constants for fairing of expansion coefficients
G_{a21}	expansion coefficient for overlap contribution to $\mu_{(1)}$, charge bohr, C m
$G_{l\mu}$	expansion coefficient for $\mu_{(1)}$, charge bohr; C m
G_{q21}	expansion coefficient for quadrupole-induced contribution to $\mu_{(1)}$, charge bohr; C m
g_{21}	coefficient for quadrupole-induced contribution to (1) component of dipole moment, charge $bohr^5$; C m^5
H_{a21}	expansion coefficient for overlap contribution to $\mu'_{(1)}$, charge; C
$H_{l\mu}$	expansion coefficient for $\mu'_{(1)}$, charge; C
H_{q21}	expansion coefficient for quadrupole-induced contribution to $\mu'_{(1)}$, charge; C
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 2π, J/sec
$J_n(\sigma)(n = 1, 2, \ldots, 5)$	function of σ
$L(\sigma,\tau)$	function of σ and τ
$M(\sigma)$	approximation to $M(\sigma,\tau)$ for small τ
$M(\sigma,\tau)$	function of σ and τ
$m_{jaa}(j = 1, 3)$	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 μ_{x_j} for H_2-H, charge bohr; C m
N_1, N_2, N_3	contributions to numerator of expression for μ_{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	intermolecular 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 τ
$T(\sigma,\tau)$	function of σ and τ
$U(\sigma)$	approximation to $U(\sigma,\tau)$ for small τ
$U(\sigma,\tau)$	function of σ and τ
X, Y, Z	Cartesian coordinates with origin at midpoint of line connecting protons a and b and with Z running along line $\overline{ab}$, 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}	x_3 component of vector from proton a to electron 1, bohr; m
x_{3ac1}	x_3 component of vector from center of line $\overline{ac}$ to electron 1, bohr; m
x_{3p}	x_3 coordinate of proton p, bohr; m
$Y_{l\mu}$	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 $\hbar/2$
α_a	polarizability of H atom a, charge^2 bohr^2 hartree^{-1}; C^2 m^2 J^{-1}
$\alpha, \alpha_{ab}, \alpha_{cd}$	average polarizability of H_2 molecule (subscripts indicate which molecule), charge^2 bohr^2 hartree^{-1}; C^2 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 H_2 molecule (subscripts indicate which molecule), charge^2 bohr^2 hartree^{-1}; C^2 m^2 J^{-1}
ζ_a	orbital exponent of H atom a, bohr^{-1}; m^{-1}
$\zeta, \zeta_{ab}, \zeta_{bc}, \zeta_{cd}$	orbital exponent of H_2 molecule (subscripts indicate which molecule), bohr^{-1}; m^{-1}
$\bar{\zeta}$	orbital exponent of two repelling H atoms used in calculating λ, bohr^{-1}; m^{-1}
$\Theta_{l\mu}$	normalized associated Legendre function
$\theta, \theta_1, \theta_2$	polar angles (see figs. 1 and 5), deg
θ_{abc}	angle between protons b and c at proton a (first or second quadrant), deg
$\theta_{abx_j}(j = 1, 3)$	angle at proton a between proton b and line through proton a parallel to the x_j axis (first or second quadrant), deg
θ_{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 H_2 molecule (subscripts indicate which molecule), bohr^{-1}; m^{-1}
λ, λ_{ab}	repulsive distortion parameter (subscripts indicate repelling orbitals), bohr^{-1}; m^{-1}
$\vec{\mu}$	dipole moment vector, charge bohr; C m

$\vec{\mu}_a$	overlap contribution to $\vec{\mu}$, charge bohr; C m
μ_{ax_j} (j = 1, 2, 3)	x_j component of $\vec{\mu}_a$, charge bohr; C m
μ_{qx_3}	x_3 component of quadrupole-induced contribution to $\vec{\mu}$, charge bohr; C m
μ_{x_j} (j = 1, 2, 3)	x_j component of $\vec{\mu}$, charge bohr; C m
$\mu_{(1)}, \mu_{(-1)}$	complex components of $\vec{\mu}$, charge bohr; C m
σ	σ_{ac} with any subscripts
σ_{ac}	r_{ac} times average value of ζ for orbitals a(1) and c(1)
τ	τ_{ac} with any subscripts
τ_{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
φ_{cabx_j} (j = 1, 3)	dihedral angle between plane cab and plane containing a, b, and line parallel to the x_j axis, deg
Ψ	antisymmetric system wave function, $bohr^{-6}$; m^{-6}
ψ_i (i = 1, 2, . . ., 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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