

Ab initio calculation of the line strengths in the electric dipole vibration-rotation spectrum of the HD molecule

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(Received 5 June 1975; revised manuscript received 9 June 1977)

The perturbation theory expression for the HD molecule vibration-rotation dipole-transition probabilities is cast into the form of an instantaneous dipole-moment function $D(R)$. Two large components of $D(R)$ can be obtained from accurately known ground-electronic-state expectation values, whereas the rest is computed by a sum-over-states procedure similar to the one we used previously for the dynamic polarizability of H_2 . From this $D(R)$ we compute dipole-transition matrix elements for the 0-0 through 6-0 vibrational bands, for all P and R branch lines with $J_i \leq 3$. Our results agree well with the recent calculations of Wolniewicz [Can. J. Phys. **53**, 1207 (1975); **54**, 672 (1976)]. They also agree well with experiment for the 1-0 through 5-0 bands, but, like the results of Wolniewicz, are a factor of approximately $\sqrt{2}$ larger than the 0-0 band results of M. Trefler and H. P. Gush [Phys. Rev. Lett. **20**, 703 (1968)].

I. INTRODUCTION

Because of nonadiabatic effects which couple the electronic and nuclear motions, the HD isotope of molecular hydrogen has an electric dipole vibration-rotation spectrum which is completely absent in the symmetric H_2 and D_2 isotopes. The first observation of such a transition was made by Herzberg¹ in 1950, and several bands were studied by Durie and Herzberg² in 1960. Intensity measurements for the pure rotation 0-0 band have been made by Trefler and Gush,³ and in the 1-0 band by Bejar and Gush.⁴ A series of recent papers by McKellar⁵ and a paper by McKellar, Goetz, and Ramsay⁶ have reported rather precise intensity measurements for several lines in the 1-0 through 5-0 vibrational bands. In addition, the 6-0 band has been observed.⁶ The dipole spectrum of HD is of astrophysical interest as a means of detecting extraterrestrial HD and of determining its abundance. The $P1$ line in the 4-0 band has been observed in the atmosphere of Jupiter by Trauger *et al.*⁷

Theoretical calculations of the dipole-transition moment were first carried out by Wick,⁸ and somewhat later by Wu⁹ and by Blinder.¹⁰ More recent calculations include those of Bunker¹¹ and of Wolniewicz and Kowalski.¹² Very recently Wolniewicz,¹³ as an extension of earlier work by Kolos and Wolniewicz,¹⁴ has carried out an elaborate perturbation-variational calculation of the dipole-transition moment for several R -branch lines in the 0-0 through 4-0 bands. These results are in generally good agreement with the experimental results of McKellar for the vibration-rotation bands, but are about 1.4 times larger than

the results of Trefler and Gush for the pure-rotation transitions. For a closely related problem, Alemar-Rivera and Ford¹⁵ have very recently completed a theoretical study of $X^1\Sigma_g^+ \leftrightarrow E, F^1\Sigma_g^+$ non-adiabatic-allowed dipole transitions in HD; observation of these transitions has been reported by Dabrowski and Herzberg.¹⁶

The calculation of Wolniewicz¹³ constitutes the best previous theoretical treatment of the vibration-rotation line strengths in HD. It is, however, limited to R -branch lines and goes only up through the 4-0 vibrational band. The probable accuracy was given as around 10^{-6} D, whereas the experimental transition moment in the 5-0 band is only on the order of 2×10^{-6} D. These calculations already involve extensive computing, and improved accuracy by using longer expansions may not be available for some time. There is also the problem of the disagreement between these calculations and experiment for the 0-0 band. In view of these remaining problems, we report in this paper a theoretical calculation of the dipole-transition moments for HD, using a method considerably different from that of Wolniewicz. A principal feature of our method and approximations is that they lead to a dipole-moment function $D(R)$, whose matrix element is then taken between initial- and final-state vibrational wave functions. A further reason for publication of our work despite the recent progress made by Wolniewicz is that the results of preliminary versions of our work have been quoted in the literature⁶; the details of the origin of these results should be made available. Two errors in the computational procedure have been corrected. The computed dipole-transition moment now agrees well with Wolniewicz for the

0-0 band transitions, and our agreement with the 1-0 through 5-0 band experiments of McKellar are a bit improved. The calculations reported here are in somewhat better agreement with McKellar⁵ and McKellar, Goetz, and Ramsay⁶ than are those of Wolniewicz.¹³ This close agreement with experiment for the higher transitions and the close agreement between quite disjoint but very thorough calculations make further measurements of the 0-0 band highly desirable.

In Sec. II the terms in the molecular Hamiltonian which give rise to the dipole-transition moment, and the perturbation theory expression for this transition moment, are briefly discussed. In Sec. III and IV the approximations are described which lead to the final expressions for the Π_u (perpendicular component) and Σ_u (parallel component) intermediate-state contributions to the dipole-transition moments. Section V describes the calculations. The results are presented and compared to previous calculations and to experiments in Sec. VI.

II. THEORY OF THE HD NONADIABATIC-ALLOWED DIPOLE-TRANSITION MOMENT

The theory of the effect being studied here has been discussed extensively in the previous theoretical work (see especially the paper by Bunker¹¹) and will be only briefly reviewed here. The total nonrelativistic Hamiltonian for HD in a static electric field is

$$H = H_0 + H', \quad (1)$$

where H_0 is the usual Born-Oppenheimer Hamiltonian and

$$H' = H'_1 + H'_2 \quad (2)$$

is the perturbation due to the external field (H'_1) and to the coupling between electronic and nuclear motions (H'_2). If \vec{E} is the external electric field, m_p and m_D are, respectively, the proton and deuteron masses, and \vec{r}_1 and \vec{r}_2 are the position vectors of the two electrons measured from the midpoint of the internuclear axis (geometrical center of the nuclei), then in atomic units

$$H'_1 = -\vec{r} \cdot \vec{E}, \quad (3)$$

where

$$\vec{r} = \vec{r}_1 + \vec{r}_2,$$

and

$$H'_2 = -(1/2\mu)\Delta_R - (1/8\mu)(\vec{\nabla}_r)^2 - (1/2\mu_a)\vec{\nabla}_R \cdot \vec{\nabla}_r, \quad (4)$$

where

$$\mu = \frac{m_p m_D}{m_p + m_D} \quad \text{and} \quad \mu_a = \frac{m_p m_D}{m_D - m_p}.$$

Note that the Δ_R term is also present in H_0 , where it is understood to operate only on the nuclear motion part of the wave function.

Treating H' as a double perturbation, the transition dipole moment between states A and B is given (to first order in H'_2) by

$$\langle \vec{\mu} \rangle_{AB} = - \sum_{N, V_N, J_N} \left(\frac{\langle \vec{r} \rangle_{AN} \langle H'_2 \rangle_{NB}}{E_B - E_N} + \frac{\langle H'_2 \rangle_{AN} \langle \vec{r} \rangle_{NB}}{E_A - E_N} \right), \quad (5)$$

where $\langle \mathcal{O} \rangle_{AB} = \langle A; V_A J_A | \mathcal{O} | B; V_B J_B \rangle$ and the eigenfunctions and energies are those of H_0 :

$$H_0 |N; V_N J_N\rangle = E(V_N) |N; V_N J_N\rangle. \quad (6)$$

Here $|N; V_N J_N\rangle$ is the usual Born-Oppenheimer product of electronic, vibrational, and rotational wave functions, and N , V_N , and J_N denote electronic, vibrational, and rotational quantum numbers, respectively. The sum over N , V_N , and J_N is a sum over all eigenfunctions of H_0 for which the matrix elements do not vanish. Such sums will throughout the paper be meant to include an integration over the nuclear-motion continuum.

The matrix element $\langle \vec{r} \rangle_{AN}$ is nonzero only if the electronic states A and N are of opposite inversion symmetry; e.g., if A and B are the $X^1\Sigma_g^+$ HD electronic ground state, then N must be of $1\Sigma_u^+$ or $1\Pi_u$ electronic symmetry. The only part of H'_2 which has nonzero matrix elements between electronic states of opposite inversion symmetry is

$$h = -(1/2\mu_a)\vec{\nabla}_R \cdot \vec{\nabla}_r. \quad (7)$$

Thus it is this nonadiabatic perturbation, which mixes some ungerade symmetry into the predominantly gerade electronic ground-state wave function, that gives rise to the dipole-transition moment of HD. The sign of the above perturbation operator is reversed from that given by Blinder,¹⁰ because, following Kolos and Wolniewicz,¹⁷ we choose \vec{R} to be $\vec{R} = \vec{R}_D - \vec{R}_P$. Here \vec{R}_P and \vec{R}_D are the proton and deuteron position vectors taken from the midpoint of the internuclear axis. In our convention, a negative component of dipole moment along the internuclear axis, $\mu_{||}$, corresponds to H^+D^- .

III. ANALYSIS OF THE PERPENDICULAR COMPONENT

The operator h of Eq. (7) has been given by Kolos and Wolniewicz¹⁷ in terms of molecular-axis fixed coordinates x , y , and z (whose origin is at the geometrical center of the nuclei) and the polar angles θ and ϕ of the molecular axis in a space-fixed coordinate system. That part of h which has nonzero matrix elements between $1\Sigma_g^+$ and $1\Pi_u$ states is

$$h_{\perp} = -\frac{1}{4\mu_a R} \left[\nabla_r^* \left(\frac{\partial}{\partial \theta} - \frac{i}{\sin \theta} \frac{\partial}{\partial \phi} - \cot \theta L_z \right) + \nabla_r^* \left(\frac{\partial}{\partial \theta} + \frac{i}{\sin \theta} \frac{\partial}{\partial \phi} + \cot \theta L_z \right) \right]. \quad (8)$$

Consider for simplicity the space-fixed Z component of $\vec{\mu}$. The first step in its evaluation is to write this component of $\vec{\mu}$, Z' , in terms of molecular-axis fixed coordinates and the angles θ and ϕ :

$$Z' = (1/\sqrt{2})(x + iy)D_{01}^{(1)}(\phi, \theta, \psi) - (1/\sqrt{2})(x - iy)D_{01}^{(1)}(\phi, \theta, \psi) + zD_{00}^{(1)}(\phi, \theta, \psi). \quad (9)$$

Only the first two terms contribute in Eq. (5) when the states N are of ${}^1\Pi_u$ symmetry. Here $D_{m_1 m_2}^{(j)}(\phi, \theta, \psi)$ is a rotation matrix as defined by Rose,¹⁸ and the angle ψ refers to rotations about the internu-

clear axis. The integrations over rotational wave functions

$$\Psi_{J\Lambda M} = \left(\frac{2J+1}{8\pi^2} \right)^{1/2} D_{M\Lambda}^{(J)}(\phi, \theta, \psi) \quad (10)$$

can now be done in Eq. (5), using Rose's expression for the integral of the product of three rotation matrices and Kolos and Wolniewicz's¹⁷ expressions for the rotational wave-function matrix elements of the operator h_{\perp} . In the sum over N , both components of the doubly degenerate Π state must be included, either by taking $\Lambda = +1$ and $\Lambda = -1$ states, or by forming the standard combinations Π^{\pm} which have definite reflection symmetry with respect to reflection in a plane containing the nuclei. If the latter is done, only the Π^+ component has nonzero h_{\perp} matrix elements with the electronic ground state. In either approach one obtains

$$\langle \mu_{\perp} \rangle_{fi} = -\frac{\delta_{M_i M_f}}{4\sqrt{2}\mu_a} \left(\frac{2J_i + 1}{2J_f + 1} \right)^{1/2} C(J_i 1 J_f; \bar{M}_i 0) \{ [J_i(J_i + 1)]^{1/2} [C(J_i 1 J_f; \bar{1} 1) + C(J_i 1 J_f; 1 \bar{1})] \alpha_{fi} + [J_f(J_f + 1)]^{1/2} [C(J_i 1 J_f; 0 \bar{1}) + C(J_i 1 J_f; 0 1)] \beta_{fi} \}. \quad (11)$$

Here f and i are used instead of A and B to refer to the initial and final states, and $C(j_1 j_2 j_3; mm')$ is a Clebsch-Gordan coefficient, as defined by Rose. We have defined

$$\alpha_{fi} = \sum_{N, V_N} \frac{\langle X; V_f | (x - iy) | N; V_N \rangle \langle N; V_N | (\nabla_r^*/R) | X; V_i \rangle}{E(V_i) - E(V_N)} \quad (12a)$$

and

$$\beta_{fi} = \sum_{N, V_N} \frac{\langle X; V_f | (\nabla_r^*/R) | N; V_N \rangle \langle N; V_N | (x + iy) | X; V_i \rangle}{E(V_f) - E(V_N)}, \quad (12b)$$

where the wave functions $|N; V_N\rangle$ are products of electronic and vibrational parts.

The sums of Clebsch-Gordan coefficients give selection rules on J . In particular, $\langle \mu_{\perp} \rangle_{fi} = 0$ if $J_i = J_f$, and is nonzero only for $J_f = J_i + 1$ (R branch) and $J_f = J_i - 1$ (P branch). Evaluating the Clebsch-Gordan coefficients we have, for the R branch,

$$\langle \mu_{\perp} \rangle_{fi}^R = \frac{1}{4\mu_a} \left(\frac{(J_i + 1) - M_i^2}{(2J_i + 1)(2J_f + 1)} \right)^{1/2} \times [(\alpha_{fi} - \beta_{fi}) - (J_i + 1)(\alpha_{fi} + \beta_{fi})]. \quad (13)$$

When one takes $\sum_{M_i} |\langle \vec{\mu} \rangle|^2$, the factor

$$\left(\frac{(J_i + 1) - M_i^2}{(2J_i + 1)(2J_f + 1)} \right)^{1/2}$$

leads to the usual $J_f + 1$ R -branch rotational line-strength factor, so we define

$$\langle D_{\perp} \rangle_{fi}^R = (1/4\mu_a) [(\alpha_{fi} - \beta_{fi}) - (J_i + 1)(\alpha_{fi} + \beta_{fi})]. \quad (14)$$

A similar analysis for the P branch yields

$$\langle D_{\perp} \rangle_{fi}^P = (1/4\mu_a) [(\alpha_{fi} - \beta_{fi}) + J_i(\alpha_{fi} + \beta_{fi})]. \quad (15)$$

This part of the problem has been reduced to the evaluation of α_{fi} and β_{fi} . As Bunker has shown,¹¹ approximate expressions for the quantities may be derived as follows. If one assumes that $[r_j, H_{BO}] \approx \partial/\partial r_j$, where $r_j = x, y, \text{ or } z$, then

$$\langle N; V_N | \nabla_j | X; V_i \rangle = [E(V_i) - E(V_f)] \langle N; V_N | r_j | X; V_i \rangle. \quad (16)$$

With this approximation the sums in Eq. (12) can be evaluated by closure, and one has

$$\alpha_{fi} \approx -\beta_{fi} \approx 2 \langle V_f | (\langle X | x^2 | X \rangle / R) | V_i \rangle. \quad (17)$$

Thus to this level of approximation the explicitly rotationally dependent terms in Eqs. (14) and (15) vanish and $\langle D_{\perp} \rangle_{fi}^{P,R}$ is given in terms of the matrix element of a dipole-moment function $D_{\perp}(R)$ between the initial and final vibrational wave functions,

where

$$D_{\perp}(R) = (1/\mu_a) \langle X | x^2 | X \rangle. \quad (18)$$

The $X^1\Sigma_g^+$ state expectation value of $x^2 = (x_1 + x_2)^2$ has been very accurately calculated as a function of R by Kolos and Wolniewicz.¹⁹

The explicitly J -dependent parts of Eqs. (14) and (15) have also been approximated by Bunker¹¹ [his $\eta(v', v)$] as

$$\frac{1}{4\mu_a} (\alpha_{fi} + \beta_{fi}) \approx -\frac{1}{2} \frac{E(V_f) - E(V_i)}{\bar{E}} \langle V_f | D_{\perp}(R) | V_i \rangle. \quad (19)$$

Here \bar{E} is an average-energy denominator, which we define by

$$\sum_N \frac{\langle X | (x - iy) | N \rangle \langle N | (x + iy) | X \rangle}{E_X(R) - E_N(R)} = \frac{2}{\bar{E}} \langle X | x^2 | X \rangle. \quad (20)$$

The $E_X(R)$ and $E_N(R)$ are electronic energies. Note that it can be shown¹¹ that $\alpha_{fi} + \beta_{fi}$ is rigorously zero for the 0-0 band. Again, the only calculation required is to compute the vibrational matrix elements of the already accurately known $D_{\perp}(R)$. It will be shown in the next section that $\bar{E} \approx 0.6$ a.u.,

$$\gamma_{fi} = \frac{1}{2\mu_a} \sum_{N, V_N} \left(\frac{\langle X; V_f | z | N; V_N \rangle \langle N; V_N | (\partial/\partial z)(\partial/\partial R) | X; V_i \rangle}{E(V_i) - E(V_N)} + \frac{\langle X; V_f | (\partial/\partial z)(\partial/\partial R) | N; V_N \rangle \langle N; V_N | z | X; V_i \rangle}{E(V_f) - E(V_N)} \right) \quad (23)$$

and

$$\zeta_{fi} = \frac{1}{4\mu_a} \sum_{N, V_N} \left(\frac{\langle X; V_f | z | N; V_N \rangle \langle N; V_N | [(\nabla_r^+ L^- - \nabla_r^- L^+)/R] | X; V_i \rangle}{E(V_i) - E(V_N)} + \frac{\langle X; V_f | [(\nabla_r^+ L^- - \nabla_r^- L^+)/R] | N; V_N \rangle \langle N; V_N | z | X; V_i \rangle}{E(V_f) - E(V_N)} \right). \quad (24)$$

Note that as for $\langle \mu_{\perp} \rangle_{fi}$, $\langle \mu_{\parallel} \rangle_{fi}$ vanishes if $J_i = J_f$. Hence HD has no permanent dipole moment, no first-order Stark effect, and no Q branch in its vibration-rotation spectrum.¹¹ Evaluation of the Clebsch-Gordan coefficients for $J_f = J_i \pm 1$ leads to

$$\langle \mu_{\parallel} \rangle_{fi}^R = \left(\frac{(J_i + 1) - M_i^2}{(2J_i + 1)(2J_f + 1)} \right)^{1/2} (\gamma_{fi} + \zeta_{fi})$$

(and a similar expression for the P branch), and hence to defining

$$\langle D_{\parallel} \rangle_{fi}^{P,R} = \gamma_{fi} + \zeta_{fi}. \quad (25)$$

The problem now is to evaluate γ_{fi} and ζ_{fi} . We choose to treat these two terms separately. Note that neither $(\partial/\partial z)(\partial/\partial R)$ nor $\nabla_r^+ L^- - \nabla_r^- L^+$ is Hermitian; only their sum is. Analysis of ζ_{fi} is rather

so that the explicitly rotationally dependent term contributes only a small amount to the total transition moment computed here (at most -0.026×10^{-4} D, for the R3 line in the 1-0 band), and note that $\langle V_f | D_{\perp}(R) | V_i \rangle$ will itself depend somewhat on J_i and J_f through the centrifugal term in the vibrational potential.

IV. ANALYSIS OF THE PARALLEL COMPONENT

That part of h which has nonzero matrix elements between $^1\Sigma_g^+$ and $^1\Sigma_u^+$ states is¹⁷

$$h_{\parallel} = -\frac{1}{2\mu_a} \left(\frac{\partial}{\partial z} \frac{\partial}{\partial R} + \frac{1}{2R} (\nabla_r^+ L^- - \nabla_r^- L^+) \right). \quad (21)$$

Here \vec{L} is the electronic angular-momentum operator, in the present molecule-fixed electronic coordinates. Again taking the space-fixed Z component of μ and integrating over the rotational wave functions, one has

$$\langle \mu_{\parallel} \rangle_{fi} = \delta_{M_i M_f} \left(\frac{2J_i + 1}{2J_f + 1} \right)^{1/2} C(J_i 1 J_f; \bar{M}_i 0) C(J_i 1 J_f; 00) (\gamma_{fi} + \zeta_{fi}), \quad (22)$$

where

straightforward. Similar to the approximation of Eq. (16), assume that

$$E(V_i) - E(V_N) \approx E(V_f) - E(V_N) \approx E_X(R) - E_N(R),$$

so that the sum over V_N can be evaluated by closure. Further note that

$$\langle X | (\nabla_r^+ L^- - \nabla_r^- L^+) | N \rangle = \langle N | (\nabla_r^+ L^- - \nabla_r^- L^+) | X \rangle - 4 \langle N | (\partial/\partial z) | X \rangle, \quad (26)$$

so that

$$\zeta_{fi} = \langle V_f | \zeta(R) | V_i \rangle, \quad (27)$$

with

$$\begin{aligned} \zeta(R) &= \zeta_1(R) + \zeta_2(R) \\ &= \frac{1}{2\mu_a R} \sum_N \frac{\langle X|z|N\rangle \langle N|(\nabla_r^* L^- - \nabla_r^- L^*)|X\rangle}{E_X(R) - E_N(R)} \\ &\quad - \frac{\langle X|z^2|X\rangle}{\mu_a R}. \end{aligned} \quad (28)$$

As for $\langle X|X^2|X\rangle$ needed for $D_{\perp}(R)$, $\langle X|z^2|X\rangle$ is very accurately known from the calculations of Kolos and Wolniewicz.¹⁹ The computation of $\zeta_1(R)$ will be described in the next section.

One possible approach to the evaluation of γ_{fi} , and the one we use, is to assume that in addition to Eq. (16) one has $[H_{BO}, \partial/\partial R] = -\partial V/\partial R$, so that

$$\gamma_{fi} = -\frac{1}{2\mu_a} \sum_{N, V_N} \left(\frac{\langle X; V_f | z | N; V_N \rangle \langle N; V_N | z (\partial V/\partial R) | X; V_i \rangle}{E(V_i) - E(V_N)} + \frac{\langle X; V_f | z (\partial V/\partial R) | N; V_N \rangle \langle N; V_N | z | X; V_i \rangle}{E(V_f) - E(V_N)} \right). \quad (31)$$

If one again assumes that the energy denominators can be approximated by electronic energy differences, then one has

$$\gamma_{fi} \approx \langle V_f | \gamma(R) | V_i \rangle \quad (32)$$

with

$$\gamma(R) = -\frac{1}{\mu_a} \sum_N \frac{\langle X|z|N\rangle \langle N|z(\partial V/\partial R)|X\rangle}{E_X(R) - E_N(R)}. \quad (33)$$

The evaluation of $\gamma(R)$ will be described in the next section.

V. COMPUTATIONAL PROCEDURE

It has been shown in the previous two sections that the HD dipole-transition moment for the P and R branches can be written as the usual rotational line-strength factor times the vibrational matrix element of a dipole-moment function:

$$\langle D \rangle_{fi} = \langle V_f | D(R) | V_i \rangle, \quad (34)$$

where

$$D(R) = D_{\parallel}(R) + D_{\perp}(R).$$

The $D_{\perp}(R)$ is defined by Eq. (18), and $D_{\parallel}(R) = \gamma(R) + \zeta_1(R) + \zeta_2(R)$ [Eqs. (28) and (33)]. By Eqs. (14), (15), and (19) there is also a small additional term in $\langle D \rangle_{fi}$ which is explicitly rotationally dependent and proportional to $\langle V_f | D_{\perp}(R) | V_i \rangle$. The ground-state matrix elements needed for $D_{\perp}(R)$ and $\zeta_2(R)$ are accurately known.¹⁹

The difficult part of the calculation is the evaluation of $\gamma(R)$ and $\zeta_1(R)$, each of which involves a sum over a complete set of eigenfunctions of symmetry ${}^1\Sigma_u^+$ of the Born-Oppenheimer electronic Hamiltonian H_e . These sums were evaluated by approximating the complete set of H_e eigenfunctions by a finite set of approximate eigenfunctions, ob-

$$\begin{aligned} [E(V_N) - E(V_i)] \langle N; V_N | (\partial/\partial R) | X; V_i \rangle \\ = -\langle N; V_N | (\partial V/\partial R) | X; V_i \rangle. \end{aligned} \quad (29)$$

Here V is the potential in the electronic part of the Born-Oppenheimer Hamiltonian, so that

$$\frac{\partial V}{\partial R} = \frac{1}{2} \left(\sum_{i=1}^2 \frac{\cos(\theta_{ai})}{r_{ai}^2} - \frac{\cos(\theta_{bi})}{r_{bi}^2} \right) - \frac{1}{R^2}. \quad (30)$$

The polar coordinates are those of each of the two electrons, in coordinate systems centered on each of the nuclei a and b . The z axis of each coordinate system points in the direction a to b . Following the analysis given by Blinder,¹⁰ one can show that

tained by matrix diagonalization of the representation of H_e on a finite basis. The finite sets of eigenvectors used were the same as were used by us to evaluate the sum-over-states formula for the dipole polarizability of H_2 ,²⁰ and contain up to 52 members. These sets of eigenvectors have the property of being complete with respect to the dipole oscillator strength. The results, along with the previously known $D_{\perp}(R)$ and $\zeta_2(R)$, are given in Table I. Our computed $D(R)$ does not have a maximum for the range of R values considered here.¹⁰

One indication that the sets of ${}^1\Sigma_u^+$ functions used form an accurate approximation to the complete set of exact Born-Oppenheimer electronic eigenfunctions is that the computed $\gamma(R)$ and $\zeta_1(R)$ are reasonably well converged with respect to increasing the size of the finite basis sets from which the approximate functions were obtained. This is illustrated in Table II. The B -state contribution is about 50% of the total for $\gamma(R)$ and about 25% for $\zeta_1(R)$.

A second check on the completeness of the set of ${}^1\Sigma_u^+$ functions is provided by setting the energy denominators in $\gamma(R)$ and $\zeta_1(R)$ equal to unity. Then the sums can be carried out exactly by closure. The resulting ground-state matrix element can be evaluated and compared to the value obtained by explicitly carrying out the summation. The results of doing this are given in Tables III and IV. It is seen that the set of ${}^1\Sigma_u^+$ functions used here forms a very good numerical approximation to a complete set for the present operators.

The accuracy to which closure is satisfied for the matrix elements over the given wave function basis also lends credence to the use of the Hellmann-Feynman theorem in the development of

TABLE I. The HD dipole-moment function in units of 10^{-4} D.

R	$D_{\perp}(R)$	$\gamma(R)$	$\xi_1(R)$	$\xi_2(R)$	$D_{\parallel}(R)$	Total $D(R)$
0.5 a_0	12.868	-26.426	-0.394	-13.438	-40.258	-27.390
0.75	9.800	-13.768	-0.738	-10.644	-25.150	-15.350
1.0	8.296	-8.747	-1.052	-9.423	-19.222	-10.926
1.2	7.539	-6.516	-1.445	-8.883	-16.844	-9.305
1.3	7.244	-5.692	-1.624	-8.690	-16.006	-8.762
1.35	7.108	-5.350	-1.707	-8.607	-15.664	-8.556
1.4	6.983	-5.028	-1.794	-8.532	-15.354	-8.371
1.45	6.864	-4.665	-1.909	-8.462	-15.036	-8.172
1.5	6.753	-4.422	-1.984	-8.397	-14.803	-8.050
1.6	6.546	-3.839	-2.189	-8.281	-14.309	-7.763
1.8	6.182	-2.926	-2.571	-8.077	-13.574	-7.392
2.0	5.865	-2.126	-2.938	-7.892	-12.956	-7.091
2.5	5.183	-0.578	-3.633	-7.347	-11.558	-6.375
3.0	4.573	+0.420	-3.708	-6.556	-9.844	-5.271

Eq. (31), since the expectation value for the ground-state function is found to be quite stable with respect to increasing the complexity of the ground-state wave function. Further confidence in the use of the Hellmann-Feynman $\langle \partial V / \partial R \rangle$ matrix elements is given by the stability of the $\gamma(R)$ sum over wave-function representations of increasing complexity.

As a further check on the accuracy of our integral evaluation programs, we repeated Blinder's calculation¹⁰ of $\gamma(R=1.4a_0)$; complete agreement was obtained. Blinder's value of $\gamma(R=1.4a_0)$ is -5.68×10^{-4} D, in fairly good agreement with the value -5.03×10^{-4} obtained with the more elaborate wave functions of the present work. It is of inter-

est to note that Blinder's set of ${}^1\Sigma_u^+$ functions give fairly good values for the moments $S(0)$, $S(-1)$, and $S(-2)$ of the parallel component of the dipole oscillator strength distribution, for $R=1.4a_0$. His wave functions give (taking the average of length and velocity formulation results) $S(0)=2.006$, $S(-1)=3.394$, and $S(-2)=6.086$. The correct values for these quantities are $S(0)=2.000$, $S(-1)=3.453$, and $S(-2)=6.380$.

The vibrational matrix elements of the $D(R)$ of Table I were computed using vibrational wave functions obtained from standard Numerov solution of the radial Schrödinger equation, using the very accurate adiabatic potential of Kolos and Wolniewicz.^{19,21} The results will be presented and discussed in the next section.

TABLE II. Convergence of the calculation of $\gamma(R)$ and $\xi_1(R)$.

R	$\gamma(R)$ (10^{-4} D)		
	$X(14\text{-term});$ ${}^1\Sigma_u^+(26\text{-term})$	$X(14\text{-term});$ ${}^1\Sigma_u^+(36\text{-term})$	$X(24\text{-term});$ ${}^1\Sigma_u^+(52\text{-term})$
1.0 a_0	-8.926	-8.792	-8.747
1.2	-6.757	-6.578	-6.516
1.4	-5.233	-5.020	-5.028
1.6	-3.925	-3.860	-3.839
2.0	-2.193	...	-2.126
3.0	+0.272	+0.400	+0.420

R	$\xi_1(R)$ (10^{-4} D)	
	$X(14\text{-term});$ ${}^1\Sigma_u^+(26\text{-term})$	$X(24\text{-term});$ ${}^1\Sigma_u^+(52\text{-term})$
1.0 a_0	-1.114	-1.052
1.2	-1.464	-1.445
1.4	-1.828	-1.794
1.6	-2.208	-2.189
2.0	-2.977	-2.938
3.0	-3.734	-3.708

VI. RESULTS AND DISCUSSION

Our $\langle D \rangle_{J,t}$ can be compared both to experiment and to the recent elaborate perturbation-variational calculations of Wolniewicz.¹³ Wolniewicz also treated the parallel and perpendicular components separately. Table V compares his results and ours for the perpendicular component. The agreement is quite good. Note that Wolniewicz states that the last figure in his result probably has little meaning. Our part with explicit J dependence is given separately. It is seen to be small, but does somewhat improve the agreement, especially in the 1-0 band. The \bar{E} required for this term was obtained from Eq. (20) by comparing $\alpha_{\perp}(R)$ (the perpendicular component of the static dipole polarizability) to $\langle x^2 \rangle$. In this way \bar{E} was estimated to be about 0.60 a.u. We emphasize that for the perpendicular component we have done really nothing new, merely making use of the analysis of Bunker¹¹ and the matrix elements of Kolos and Wolniewicz.¹⁹ A similar comparison is given in

TABLE III. Completeness test for $\gamma(R)$. $L = -\langle X|z^2(\partial V/\partial R)|X\rangle$ and $M = -\sum_N \langle X|z|N\rangle \langle N|z|\partial V/\partial R|X\rangle$, both in a.u.

R	L		M		
	X(14-term)	X(24-term)	X(14-term); ${}^1\Sigma_u^+$ (26-term)	X(14-term); ${}^1\Sigma_u^+$ (36-term)	X(24-term); ${}^1\Sigma_u^+$ (52-term)
1.0 a_0	0.896	0.894	0.906	0.901	0.899
1.2	0.613	0.610	0.622	0.618	0.614
1.4	0.431	0.434	0.436	0.436	0.436
1.6	0.310	0.310	0.326	0.314	0.312
2.0	0.156	0.157	0.170		0.159

Table VI for the parallel component. The agreement is again rather good, if one again notes that the last figure in the Wolniewicz calculation is said by him to have little meaning. For both the parallel and perpendicular components, the agreement does become worse in the higher vibrational bands. The accuracy of Wolniewicz's perturbation-variational calculation surely becomes worse for higher V_f , and both calculations suffer from increased cancellation for higher ΔV .

The accuracy of the present calculation is difficult to assess, as errors come not only from the incomplete set of states used for $\gamma(R)$ and $\zeta_1(R)$, but also from the approximations used to derive the form of $D(R)$. In Table VII we give the various components of our $\langle D \rangle_{fi}$ for the R0 lines, so one can see their relative importance. Except for the 0-0 band, γ_{fi} to a large extent dominates.

In Table VIII our results for $\langle D \rangle_{fi}$ are compared to experiment. The calculations of Wolniewicz are also included in the comparison. It can be seen that for the 0-0 band the two calculations agree very well with each other, but are about $\sqrt{2}$ times larger than the experimental results of Treffler and Gush.³ Another experimental measurement of the 0-0 band line intensities would thus be of great interest. For the other bands the agreement is rather good, although in some instances our results are somewhat outside the experimental error limits. Our results are in general closer to the experimental values than are

those of Wolniewicz, but in the absence of any quantitative error estimate in our calculation one cannot say with any assurance that this is of any real significance. Note, however, that our results continue to agree well with experiment up through the 5-0 band. Also note that the rotational dependence in the 1-0 band is very similar in our and Wolniewicz's calculations, but does not agree very well with that of McKellar. In Table IX we tabulate our dipole-transition matrix elements for vibrational bands up through 6-0 and through the P3 and R3 rotational lines.

The present results differ quantitatively from our earlier unpublished calculation. The difference between the present results and those quoted by McKellar *et al.*⁶ as "Ford and Browne (1975)" is due to the following: (1) Our earlier work had an algebraic error in the analysis that led to $D_1(R)$; this error results in a $D_1(R)$ smaller by $\sqrt{2}$ from the present one. (2) In our earlier preliminary work, the $\nabla_r^+ L^- - \nabla_r^- L^+$ operator was treated as if it were Hermitian; as a result we missed the $\zeta_2(R)$ term of the present calculation.

In summary, we have evaluated the HD dipole-transition moment using a sum-over-states procedure similar to that used previously for the dynamic polarizability of H_2 .²⁰ The analysis we use casts the problem in terms of a dipole-moment function $D(R)$, two large components of which can be obtained from accurately known ground-state expectation values. Our results agree well with

TABLE IV. Completeness test for $\zeta_1(R)$. $L = \langle X|z(\nabla^+ L^- - \nabla^- L^+)|X\rangle$ and $M = \sum_N \langle X|z|N\rangle \langle N|(\nabla^+ L^- - \nabla^- L^+)|X\rangle$, both in a.u.

R	L		M	
	X(14-term)	X(24-term)	X(14-term) ${}^1\Sigma_u^+$ (26-term)	X(24-term) ${}^1\Sigma_u^+$ (52-term)
1.2 a_0	0.459		0.451	0.454
1.4	0.572	0.565	0.546	0.559
1.45	0.600		0.604	0.590
1.6	0.686		0.684	0.670
2.5	1.030		1.026	1.016

TABLE V. Comparison of theoretical values for $\langle D_{\perp} \rangle_{fi}$, in units of 10^{-4} D.

	Wolniewicz ¹³	Present calculation		
		1st term in Eq. (14)	2nd term	Total
0-0 band				
R0	6.91	6.91	0.0	6.91
R1	6.90	6.91	0.0	6.91
R2	6.89	6.90	0.0	6.90
R3	6.88	6.88	0.0	6.88
1-0 band				
R0	-0.398	-0.395	-0.005	-0.400
R1	-0.445	-0.429	-0.011	-0.440
R2	-0.492	-0.462	-0.019	-0.481
R3	-0.536	-0.494	-0.026	-0.520
2-0 band				
R0	0.090	0.094	0.003	0.097
R1	0.103	0.103	0.006	0.109
R2	0.117	0.111	0.009	0.120
R3	0.130	0.119	0.013	0.132
3-0 band				
R0	-0.029	-0.033	-0.001	-0.034
R1	-0.034	-0.036	-0.003	-0.039
R2	-0.039	-0.039	-0.005	-0.044
R3	-0.044	-0.041	-0.006	-0.047
4-0 band				
R0	0.011	0.014	0.001	0.015
R1	0.013	0.015	0.002	0.017
R2	0.016	0.016	0.002	0.018
R3	0.018	0.017	0.003	0.020

TABLE VI. Comparison of theoretical values for $\langle D_{\parallel} \rangle_{fi}$, in units of 10^{-4} D.

	Wolniewicz ¹³	Present calculation
0-0 band		
R0	-15.27	-15.22
R1	-15.28	-15.21
R2	-15.28	-15.18
R3	-15.29	-15.14
1-0 band		
R0	0.996	0.960
R1	1.073	1.034
R2	1.148	1.104
R3	1.221	1.170
2-0 band		
R0	-0.250	-0.289
R1	-0.269	-0.308
R2	-0.287	-0.326
R3	-0.304	-0.342
3-0 band		
R0	0.129	0.116
R1	0.136	0.123
R2	0.142	0.129
R3	0.147	0.134
4-0 band		
R0	-0.066	-0.054
R1	-0.069	-0.057
R2	-0.070	-0.060
R3	-0.071	-0.062

the recent theoretical calculations of Wolniewicz, and with experiment for the 1-0 through 5-0 bands. For the 0-0 band our results agree very well with those of Wolniewicz, but are therefore about a factor of $\sqrt{2}$ larger than the experimental values of Trefler and Gush. We do not know the reason for the discrepancy, but urge that additional experimental and theoretical checks be made.

ACKNOWLEDGMENTS

This work was supported at the University of Texas by the Robert A. Welch Foundation of Hous-

TABLE VII. Comparison of the various components of $\langle D_{\parallel} \rangle_{fi}$, for the R0 line and in units of 10^{-4} D.

Band	γ	ξ_1	ξ_2	Total
0-0	-4.83	-1.89	-8.50	-15.22
1-0	0.984	-0.282	0.258	0.960
2-0	-0.253	0.031	-0.067	-0.289
3-0	0.093	-0.004	0.027	0.116
4-0	-0.045	0.003	-0.012	-0.054

TABLE VIII. Comparison between experimental and theoretical dipole-transition moments, in units of 10^{-4} D.

	Experimental		Theoretical	
	Trefler and Gush ³		Present calculation	Wolniewicz ¹³
0-0 band				
R0	5.42		8.31	8.36
R1	5.52	mean value is	8.30	8.38
R2	6.18	5.85±0.17	8.28	8.39
R3	6.41		8.26	8.41
1-0 band				
	Bejar and Gush ⁴		McKellar ⁵	
P3		0.330±0.04	0.401	
P2		0.405±0.03	0.445	
P1		0.450±0.03	0.485	
R0	0.42±0.08	0.515±0.02	0.560	0.598
R1	0.68±0.12	0.550±0.03	0.594	0.628
R2		0.615±0.03	0.623	0.656
R3	0.72±0.14	0.655±0.04	0.650	0.685
2-0 band				
	McKellar ⁵			
P1	0.17±0.02		0.176	
R0	0.19±0.02		0.192	0.160
R1	0.20±0.02		0.199	0.166
3-0 band				
	McKellar ⁵			
R0	0.0795±0.0035		0.082	0.100
R1	0.0800±0.005		0.084	0.102
4-0 band				
	McKellar <i>et al.</i> ⁶		McKellar ⁵	
P1	0.0397±0.0026	0.0464±0.0033	0.038	
R0	0.0417±0.0024		0.039	0.056
R1	0.0425±0.0021		0.040	0.056
R2	0.0459±0.0026		0.042	0.055
R3	0.0514±0.0053		0.042	0.053
5-0 band				
	McKellar <i>et al.</i> ⁶			
R0	0.0207±0.0020		0.023	
R1	0.0214±0.0014		0.023	
R2	0.0231±0.0021		0.024	

TABLE IX. Dipole-transition moments of HD, in units of 10^{-4} D.

Band	Line						
	P3	P2	P1	R0	R1	R2	R3
0-0	-8.282	-8.297	-8.306	-8.306	-8.297	-8.282	-8.262
1-0	+0.401	+0.445	+0.485	+0.560	+0.594	+0.623	+0.650
2-0	-0.156	-0.167	-0.176	-0.192	-0.199	-0.206	-0.210
3-0	+0.068	+0.072	+0.076	+0.082	+0.084	+0.085	-0.087
4-0	-0.033	-0.035	-0.038	-0.039	-0.040	-0.042	-0.042
5-0	+0.020	+0.021	+0.021	+0.023	+0.023	+0.024	+0.024
6-0	-0.012	-0.012	-0.013	-0.014	-0.014	-0.014	-0.015

ton, Texas, and by the Office of Naval Research under Contract No. N00014-67-A-0126-0017. Part of this work was carried out by A.L.F. at the Center for Astrophysics, where it was supported

by the National Aeronautics and Space Administration under Grant No. NGR-39-011-134. We acknowledge helpful communications with P. R. Bunker and A. R. W. McKellar.

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