Rototranslational absorption spectra of H$_2$-H$_2$ pairs in the far infrared

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For the computation of the induced dipole moments, the collisional H$_2$-H$_2$ complex is treated as a molecule in the self-consistent field and size-consistent, coupled electron pair approximations. The basis set accounts for 95% of the correlation energies and separates correctly at distant range. The average of the induced dipole components is obtained for the case of both H$_2$ molecules in the vibrational groundstate ($v'=u'=0$) and recast in a simple but accurate analytical form. The analytical dipole expression is used for computations of the spectral moments (sum rules) and line shapes of the collision-induced rototranslational absorption spectra of molecular hydrogen in the far infrared, over a range of frequencies from 0 to 2200 cm$^{-1}$, and for temperatures from 77 to 300 K, using a quantum formalism. Proven isotropic potential models are input. Numerical consistency of the line-shape calculations with the sum rules is observed at the 1% level. The comparison of the computational results with the available measurements shows agreement within the estimated uncertainties of the measurements of typically better than 10%. This fact suggests that the theory is capable of predicting these spectra reliably at temperatures for which no measurements exist.

I. INTRODUCTION

Homonuclear molecules like hydrogen in the electronic ground state are nonpolar and hence infrared inactive. Welsh and co-workers have shown, however, that compressed hydrogen gas absorbs infrared radiation due to the dipole moments induced by molecular interactions. The details of such collision-induced absorption (CIA) are well understood. Traditionally, the connection of theory with spectroscopic measurements has been made via two spectral moments of the lowest order which, in essence, represent total intensity and spectral width of the basic spectral line profile. For nearly classical systems, i.e., for massive collisional pairs at high temperature, these moments are easily computed from the induced dipole components and interaction potential on the basis of a classical formalism with lowest-order quantum corrections. However, recent interest in the accurate modeling of radiative transfer in the atmospheres of the outer planets requires accurate knowledge of the temperature dependence of the rototranslational (RT) spectral profiles. We thus report here rigorous line-shape computations of the CIA RT spectra of hydrogen from first principles. We note that, at the temperatures of interest (40–300 K), the H$_2$-H$_2$ pair cannot be considered a classical system, and both line-shape and moment computations must be based on quantum theory, which introduces some complexity into such calculations.

By combining quantum computations of the translational CIA spectra of hydrogen with empirically modeled rotational $S_0(0)$ and $S_0(1)$ profiles, Trafton was able to show that the infrared opacities of the atmospheres of the outer planets are largely due to the CIA RT spectra of hydrogen pairs. For the modeling of radiative transfer in such atmospheres, one needs to generate these spectra as function of temperature over a wide frequency band. While a strictly empirical temperature interpolation of measured spectra is feasible, we feel that the theoretical evaluation from first principles is required for accurate extrapolation of the absorption coefficient to temperatures where measurements are not available. Furthermore, from the point of view of the molecular scientist, a critical comparison of fundamental theory and measurement is best based on the full RT spectral profile with its many discriminating features, slopes, curvatures, spectral widths, and dimer line structures, rather than on merely two numbers, the zeroth and first spectral moments, which have less discriminating capability. An adiabatic theory of CIA RT spectral profiles was previously communicated for the somewhat simpler H$_2$-He system, and the present work may be considered its natural extension to the H$_2$-H$_2$ pair. The theory as presented here is, of course, more generally applicable to diatomic and linear symmetric molecules if the induced dipole components are known.

II. LINE-SHAPE THEORY

The absorption coefficient at the temperature $T$ and angular frequency $\omega = 2 \pi c v$ arising from collision-induced dipoles in molecular pairs at low densities can be written as

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\[ \alpha(\omega; T) = \frac{2\pi^2}{3\hbar c} n^2 \omega (1 - e^{-\omega/kT}) \mathcal{V}g(\omega; T), \]  

where \( n \) is the number density of the gas, \( \mathcal{V} \) is the volume, and \( T \) is the temperature. The density \( n \) is often expressed in units of amagat, in which case \( n \) is equal to \( n_{\text{amagat}} = 2.68675 \times 10^{19} \text{ cm}^{-3} \text{ amagat}^{-1} \) being Loschmidt's number. The spectral density \( g(\omega; T) \) is defined in terms of the matrix elements of the induced electric dipole moment \( \mu \) by the "golden rule;"

\[ g(\omega; T) = \sum_{s,t} P_s \sum_{s'} P_{s'} | \langle s | \mu_{\omega} | t' \rangle |^2 \delta(\omega_{s,s'} + \omega - \omega). \]

The subscripts \( s = \{ j_1, m_1, v_1, j_2, m_2, v_2 \} \) and \( t = \{ l, m_l, E_l \} \) denote molecular and translational states, respectively; the \( j,m \) refer to rotational states and the \( v \) to vibrational states, the subscripts 1 and 2 refer to molecules 1 and 2, and a prime denotes final states. The normalized translational Boltzmann factor is given by

\[ P_j(T) = \lambda_0^3 V - \frac{E_j}{kT} \quad \text{ with } \lambda_0 = \left( \frac{2\pi \hbar^2}{mkT} \right)^{1/2}, \]

where \( \lambda_0 \) is the thermal de Broglie wavelength. The rotational Boltzmann factor is written as \( P_j(T) = P_{j_1}(T)P_{j_2}(T) \), with

\[ P_j(T) = \frac{g_j \exp(-E_j/kT)}{\sum_j g_j (2J+1) \exp(-E_j/kT)}. \]

The nuclear weights of hydrogen are \( g_j = 1 \) for even \( j \), and \( g_j = 3 \) for odd \( j \). However, we mention that in low-temperature laboratory measurements as well as in astrophysical applications, para-H\(_2\) and ortho-H\(_2\) abundances may differ from the proportions characteristic for thermal equilibrium [Eq. (4)]. In such case, at any fixed temperature \( T \), one may account for nonequilibrium proportions by assuming \( g_j \) values so that the ratio \( g_0/g_1 \) reflects the actual para-to-ortho abundance ratio. Positive frequencies correspond to absorption, while the spectral function \( g(\omega; T) \) is also defined for negative frequencies which correspond to emission. We note that the separability of the translational states from the rotovibrational states requires that the potential be isotropic. For H\(_2\) this is nearly true. Although the potential function has appreciable anisotropic terms, the rather large rotational quanta of H\(_2\) ensure the neglect of these terms to be a good approximation which we will use throughout the work. We note, furthermore, that the product \( Vg(\omega; T) \) actually does not depend on \( V \) because of the reciprocal \( V \) dependence of \( P_j \) [Eq. (3)].

The induced dipole moment \( \mu \) is expressed in the form

\[ g(\omega; T) = \sum_{\lambda_1,\lambda_2,\lambda_{\Omega}} \sum_{j_{1'},j_{2'},j_{1},j_{2}} (2j_1 + 1)P_{j_{1'}}(C(j_1\lambda_1j_{1'};0000)(2j_2 + 1)P_{j_{2'}} C(j_2\lambda_2j_{2'};0000)^2 G(\lambda_1,\lambda_2,\lambda_{\Omega};\omega - \omega_{j_{1'}} - \omega_{j_{2'}};T). \]

In the isotropic potential approximation, the complete spectrum is obtained by superimposing basic line profiles, which we will refer to as translational components, \( G_{\lambda_1,\lambda_2,\lambda_{\Omega}}(\omega; T) \); these are shifted by sums of molecular ro-
\[ V_{\lambda_1 \lambda_2 \lambda \Lambda L}(\omega ; T) = \lambda_1 \lambda_2 \lambda \Lambda L \sum_{l', l} \left( 2l + 1 \right) C(lLl'; 000) \sum_{j_1 j_2} (2l + 1) C(lLl'; 000) \sum_{j_1 j_2} \right) \\
\times \left[ \int_0^\infty \exp \left( -E_i/kT \right) dE_i \left\langle \langle l, E_i | B_{\lambda_1 \lambda_2 \lambda \Lambda L}(R) | l', E_i + \hbar \omega \rangle \right\rangle \right]^2 \\
+ \sum_{n, n'} \exp \left( -E_{nl}/kT \right) \left\langle \langle l, E_{nl} | B_{\lambda_1 \lambda_2 \lambda \Lambda L}(R) | l', E_{n'l'} \rangle \right\rangle^2 \delta(E_{n'l'} - E_{nl} - \hbar \omega) \\
+ \sum_{n} \exp \left( -E_{nl}/kT \right) \left\langle \langle l, E_{nl} | B_{\lambda_1 \lambda_2 \lambda \Lambda L}(R) | l', E_{n'l'} + \hbar \omega \rangle \right\rangle^2 \\
+ \sum_{n'} \left\langle \langle l, E_{n'l'} - \hbar \omega | B_{\lambda_1 \lambda_2 \lambda \Lambda L}(R) | l', E_{n'l'} \rangle \right\rangle^2 \right\rangle \\
. \tag{10} \]

In this expression, the \( \langle \cdots \rangle \) represent radial matrix elements,

\[ \langle l, E | B | l', E' \rangle = \int_0^\infty \psi^*(R ; l, E') B(R) \psi(R ; l, E) dR , \tag{11} \]

with functions \( \psi \) defined below. The \( w(\cdots) \) designate a weight which accounts for the molecular interchange symmetry. At low temperatures, para- and ortho-H\(_2\) molecules are all in the \( j = 0 \) and \( j = 1 \) state, respectively, and the weight can be expressed in terms of a symmetry parameter \( \gamma_S \), according to \( w = 1 + \left( -1 \right)^{\gamma_S} \). In this case, in pure para-hydrogen, \( \gamma_S = 1 \) and only even parabola waves occur in Eq. (10). In general, however, a smaller \( \gamma_S \) value is called for. In Appendix A we give the relationships between \( \gamma_S \) and the para- and ortho-H\(_2\) abundances for low temperatures. However, as we will see below, for the low-resolution CIA RT spectra, this symmetry only matters at temperatures much lower than 40 K; only the generally weak dimer structures are discernibly affected by symmetry. At temperatures above 40 K one may assume \( w = 1 \) and \( \gamma_S = 0 \).

The expression to the right-hand side of Eq. (10) consists of a sum of four terms. The first term, the integral, represents the free-transitions of the collisional pair and is usually the dominant term in this expression. The second term, a sum, gives the bound-transitions of the van der Waals dimers. The vibrational and rotational quantum numbers of the dimer are designated by \( n \) and \( l \); \( l \) also numbers the partial waves. For practical purposes, one will convolute the \( \delta \) function with some suitable instrumental or line profile for a more realistic simulation of the observation. The last two terms to the right-hand side of Eq. (10) account for bound-free and free-bound transitions of the molecular pair, respectively. We note that the energies \( E_{nl} + \hbar \omega \) and \( E_{n'l'} - \hbar \omega \) appearing in these terms must be legitimate free-energy states, i.e., they must be positive or else the radial matrix elements vanish.

The radial wave functions \( \psi(R ; l, E_i) \) needed for the computation of Eq. (10) are solutions of the Schrödinger equation of relative motion of the molecular pair,

\[ -\frac{\hbar^2}{2m} \frac{d^2}{dR^2} + \left( V_0(R) + \frac{\hbar^2 l(l+1)}{2mR^2} - E_i \right) \psi = 0 , \tag{12} \]

where \( V_0(R) \) is the interaction potential. For easy integration of Eq. (10), free-state wave functions are energy normalized,

\[ \int_0^\infty \psi^*(R ; l, E_i) \psi(R ; l, E_i) dR = \delta(E_i - E_i) \tag{13} \]

for any fixed \( l \). For bound states, the \( \delta \) function in Eq. (13) is replaced by the Kronecker \( \delta \) symbol, \( \delta_{nn'} \); as usual; \( E_i \) is then replaced by \( E_{nl} \) which is negative. We note that the integration over predissociating states in the first term to the right of Eq. (10) must be done with carefully tailored energy grids. Third-order spline integration gives the necessary flexibility, and satisfactory results are obtained for a truncated integration interval, from \( E_i = kT/100 \) (instead of 0) to \( \approx 15kT \) (instead of \( \infty \)). Similarly, the radial integrals \( \langle lE | B | l'E \rangle \) can be simply truncated at an \( R_{\text{max}} \) of 12–20 Å.

The spectral function, Eq. (10), and thus the absorption coefficient, Eqs. (1) and (9), can be computed if an interaction potential and the significant induction operator components are known. The spectral function, Eq. (9), consists of a number of lines at rotational transition frequencies of the monomers \( j_1 \neq j_1' \) or \( j_2 \neq j_2' \) lines at sums and differences of such rotation frequencies (both \( j_1 \neq j_1' \) and \( j_2 \neq j_2' \)), and a translational component \( j_1 = j_1' \) and \( j_2 = j_2' \). Equation (9) shows how the \( \lambda_1 \lambda_2 \) impose selection rules on the molecular transitions, and Eq. (10) shows how the expansion parameter \( L \) controls translational transitions through basic properties of the Clebsch-Gordan coefficients; \( C(jj'; 000) = 0 \) unless the value of the sum of \( j, \lambda, \) and \( j' \) is an even integer and the triangular inequalities are satisfied. After a suitable choice of an interaction potential model, radial wave functions are obtained at 3000 grid points with the Numerov algorithm. For the spectral functions \( V_{\lambda_1 \lambda_2 \lambda \Lambda L} \), 5000 radial matrix elements, \( \langle lE | B | l'E \rangle \), are computed at the temperature of 50 K, and more for the higher temperatures, for a numerical precision of \( \approx 1\% \). This is by far the most computation-intensive part of the work. All the other calculations required for a line-shape computation take just seconds.

### III. Spectral Moments

The theory of spectral moments is described elsewhere.\(^\text{3,4}\) The translational moments are integrals of Eq.
(10) with respect to angular frequency,

$$M_n(T; \lambda_1, \lambda_2; \Delta L) = \int_{-\infty}^{\infty} V G_{\lambda_1, \lambda_2; \Delta L}(\omega; T) \omega^n d\omega.$$  (14)

For \( n = 0, 1, 2 \), these can also be computed directly from the potential function and induction operator using well-known sum rules.\(^4,\(^13\) The latter are computed in a fraction of the time required for line-shape calculations and offer a desirable test of the numerical precision attained in the line-shape calculations. Since hydrogen pairs at the temperatures of interest must be considered wave-mechanical systems, an exact quantum formalism is used for the computation of the sum rules which is described elsewhere.\(^14\) If the sum formulas are combined with suitable model profiles, complete RT CIA spectra that approximate the exact line-shape calculations closely can be generated with ease.\(^15,\(^16\)

Other moments often specified in experimental investigations are certain integrals of the RT spectra, namely,

$$\gamma_i = \frac{\hbar}{2kT} \frac{1}{n^2} \int_0^\infty \frac{\alpha(\omega; T) d\omega}{\omega \tanh(\hbar \omega / 2kT)},$$  (15)

and

$$\alpha_i = \frac{1}{n^2} \int_0^\infty \alpha(\omega; T) d\omega.$$  (16)

These moments, also called spectral invariants, are functions of temperature and will also be obtained here from the computed \( \alpha(\omega; T) \) for a comparison with the measurements.

**IV. THE \textit{ab initio} INDUCED DIPOLE**

Collisonally induced dipole moments arise from three mechanisms: induction due to static multipole moments, charge distortions due to electron exchange, and dispersion forces. Their \textit{ab initio} calculation poses problems similar to those known from the calculation of van der Waals potentials. For the most relevant molecular separations, i.e., around the collision diameter, the induced moments are rather small, but perturbation theory fails to adequately handle the exchange contribution which become large at such short distances. It appears therefore best to treat the collisional complex as a supermolecular in self-consistent-field (SCF) and configuration interaction (CI) calculations, provided that the basis set superposition error is effectively controlled and the CI excitation level is adequate for the long-range effects.

We note that induced dipole moments of \( \text{H}_2-\text{H}_2 \) pairs were previously computed from first principles.\(^17\) This early work was, however, limited to small separations and to an internuclear distance of the \( \text{H}_2 \) molecules of 1.401 Bohr. Near the separation of \( R = 4.5 \) Bohr, those computations are in reasonable agreement with the quadrupole-induced component but depart rapidly from it with increasing \( R \).

Electron correlation effects on the induced dipole moments and the computational procedures involved have been discussed in detail previously by Meyer.\(^18\) The preliminary results communicated previously\(^18\) for the \( \text{H}_2-\text{H}_2 \) system are fully corroborated by the present, extended study. It was shown in Ref. 18 and also in recent work on \( \text{H}_2-\text{He} \) and \( \text{H}_2-\text{Ar} \) (Refs. 9 and 19) that a standard singles plus doubles CI (or corresponding pair treatment) is insufficient for systems involving \( \text{H}_2 \). This is due to the fact that the quadrupole moment of \( \text{H}_2 \) is in error by 8% for an SCF wave function, and by 4% if the SCF orbital is replaced by the principal natural orbital. Thus, \( \text{H}_2 \) has to be described by a wave function including the leading double substitutions, and the proper inductive response of the collisional partner requires either triple substitutions or a multiconfiguration-reference CI. Our preliminary calculations,\(^18\) as well as the recent calculations for \( \text{H}_2-\text{He} \) and \( \text{H}_2-\text{Ar} \), have been based on the latter method. However, when extending the set of molecular geometries for \( \text{H}_2-\text{H}_2 \) to one of no symmetry and short separations, we encountered problems with a stable definition of localized orthogonal MC-SCF orbitals, resulting in numerical noise for the smaller components of \( B \). For the present calculations we have, therefore, adopted the alternative procedure of including triple substitutions with respect to the SCF wave functions. The main dipole components appear little affected by this change of computational procedure. In all other aspects, our present calculations follow the procedures used in Refs. 9, 18, and 19.

The basis set of Gaussian type functions used here is identical to the set given in Table 1 of Ref. 9. This mixed two-center—one-center basis has been designed to account accurately for the properties of \( \text{H}_2 \) pertinent here, i.e., its low-order multipole moments, \( q_2, q_4 \), and various polarizability components, \( \alpha \). This is shown below, Table 4. The theoretical values refer to calculations performed for a \( \text{H}_2 \) bond distance of \( \langle r \rangle = 1.449 \) Bohr, the mean bond distance for zero point vibration. As we have argued in our earlier work on van der Waals coefficients,\(^20\) using this distance effectively accounts for zero point vibrational averaging. Indeed, when investigating collision induced vibrational excitations in the \( \text{H}_2-\text{He} \) system,\(^21\) we could compare zero point averaged dipoles obtained from a dipole fit to values at three \( \text{H}_2 \) bond distances with the ones computed at the mean distance \( \langle r \rangle \). The differences are less than 1% for large intermolecular separations and remain below 2% even at very short distances.\(^8\) Thus, throughout this work we make use of the \textit{"r-centroid"} approximation for vibrational averaging,

$$B_{\lambda_1, \lambda_2; \Delta L}(R) \approx A_{\lambda_1, \lambda_2; \Delta L}(\langle r_1 \rangle, \langle r_2 \rangle, R).$$  (17)

It should be noted here that vibrational averaging is mandatory since the quadrupole moment and polarizability of \( \text{H}_2 \) are rather strongly dependent on the bond distance. For the specified basis, superposition errors are in the order of 1%, but they are effectively excluded by projecting the correlation orbitals for intramolecular electron pairs onto the local molecular basis. We further note that calculations with various extended basis sets did not lead to dipole moment changes larger than 1%.

Starting from a set of 18 relative orientations of the \( \text{H}_2-\text{H}_2 \) pair, we found that only the following eight leading terms could be determined with sufficient numerical significance by a least-squares fitting:
\[ B_{2023}(R) = -B_{0223}(R), \quad B_{2021}(R) = -B_{0221}(R), \]
\[ B_{2223}(R), \quad B_{2211}(R), \quad B_{4045}(R) = -B_{0445}(R). \]

The last three of these are already smaller than the leading quadrupole-induced terms \((AL = 23)\) by nearly two orders of magnitude. The set of orientations could be reduced to just five without significant changes in the leading five components. In the process, the smallest component \(B_{2211}\) varied by about 15\% which has no discernible effect on the computed spectra.

Our final set of calculations has been performed for the six nonequivalent orientations with nonvanishing dipole moments associated with values of \(0^\circ, 45^\circ, 90^\circ, 135^\circ\) of the angles subtended by \(\hat{r}_i\) and \(\hat{R}\), and with the dihedral angle between the planes \(\hat{r}_1, \hat{R}\) and \(\hat{r}_2, \hat{R}\) of \(0^\circ\) and \(90^\circ\). This set provides nine nonredundant Cartesian dipole components. They are collected for nine intermolecular separations in Table I.

The results of least-square fits of these data to the expansion, Eq. (5), truncated after eight terms with the five independent coefficients listed as Eq. (18), are given in Table II and displayed in Fig. 1. The orientations are weighted according to the volume elements which they represent in an integration of the spheres (Ref. 22, p. 184), but different weights apparently have little effect on the results. Likewise, the extension of the expansion by the terms \(B_{4265}\) and \(B_{4245}\) and their symmetry counterparts has an insignificant effect on the other terms, again with the exception of the smallest term, \(B_{2211}\), which is then reduced by about 10\%. The added components are found to be insignificant.

For the calculation of the spectral profiles an analytical form of the expansion coefficients \(B_{\lambda, \lambda, AL}(R)\) is desirable. The numerical results are described quite accurately by a function of the form

\[ B_c(R) = \frac{B_c^{(n)}}{R^n} + B_c^{(0)} \exp\left[a_c(R - R_0) + b_c(R - R_0)^2\right], \]

where the subscript \(c\) symbolizes \(\lambda, \lambda, AL\). Equation (19) is a slight generalization of a similar form in general use. The parameter \(R_0 = 6\) bohr has been chosen to be close to the collision diameter so that \(B_c^{(0)}\) gives the approximate size of the exchange and distortion dipole contribution at the collision diameter. \(B_c^{(n)}\) accounts for the long-range induction or dispersion contributions, with \(n\) value appropriate for the leading term [see Eq. (20) below]. It should be noted that the parameter \(B_c^{(n)}\) comprises contributions from higher-order terms that are effective at the distances from 7 to 9 bohr, while the damping of the long-range terms, which is relatively large only for the weak dispersion term, is absorbed in the second term of Eq. (20). The parameters of the fit are collected in Table III. Since intermolecular separations of 3.5 bohr are not significant for the computation of the rototranslational spectra, we have excluded this distance from the fit. For

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\(^{a}(0^\circ; 0^\circ; 90^\circ; 0^\circ).\)
\(^{b}(45^\circ; 0^\circ; 135^\circ; 0^\circ).\)
\(^{c}(0^\circ; 0^\circ; 135^\circ; 0^\circ).\)
\(^{d}(90^\circ; 0^\circ; 135^\circ; 0^\circ).\)
\(^{e}(45^\circ; 0^\circ; 90^\circ; 0^\circ).\)
\(^{f}(45^\circ; 45^\circ; 135^\circ; 45^\circ).\)
TABLE II. Dipole moment expansion coefficients $B_{\lambda_1, \lambda_2, \lambda_3 L}(R)$, in $10^{-4}$ a.u., at various separations $R$.

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<td>9744</td>
<td>-2200</td>
<td>-962</td>
<td>-91</td>
<td>449</td>
</tr>
<tr>
<td>5.5</td>
<td>5312</td>
<td>-980</td>
<td>-689</td>
<td>-43</td>
<td>242</td>
</tr>
<tr>
<td>6.0</td>
<td>3684</td>
<td>-433</td>
<td>-503</td>
<td>-20</td>
<td>135</td>
</tr>
<tr>
<td>7.0</td>
<td>1937</td>
<td>-85</td>
<td>-281</td>
<td>-4</td>
<td>47</td>
</tr>
<tr>
<td>8.0</td>
<td>1118</td>
<td>-20</td>
<td>-167</td>
<td>-1</td>
<td>19</td>
</tr>
<tr>
<td>9.0</td>
<td>691</td>
<td>-6</td>
<td>-104</td>
<td>0</td>
<td>9</td>
</tr>
</tbody>
</table>

The remaining eight distances, the four-parameter analytical fit, Eq. (19), reproduces the input data of Table II to better than 0.5% for the three leading components, and to better than 3% for the remaining small ones.

The long-range induction contributions are determined by the multipole moments and polarizabilities of $H_2$. Expressions for the three leading terms have been given by Poll and Hunt.\(^4\) We give a general formula for higher-order terms, and for those terms connected with the mixed dipole-octopole polarizabilities. A derivation of this general expression is presented in Appendix B. Observing the symmetry restriction on the indices $\lambda_1, \lambda_2, \lambda_3, \lambda$, and $L$ discussed above, one finds the nonvanishing, low-order asymptotic terms as

$$B_{2023}(R) = -B_{0223}(R) \rightarrow \sqrt[3]{3} \alpha q_2 / R^4,$$

$$B_{2233}(R) \rightarrow \left( \frac{1}{3} \right)^{1/2} \gamma q_2 / R^4,$$

$$B_{4045}(R) = -B_{0445}(R) \rightarrow \sqrt[5]{5} \alpha q_4 / R^6,$$

$$B_{4245}(R) = -B_{2445}(R) \rightarrow \left[ \frac{1}{15} \right]^{1/2} \gamma q_4 - \left( \frac{1}{3} \right)^{1/2} \alpha_{134} q_2 / R^6,$$

$$B_{4265}(R) = -B_{2465}(R) \rightarrow \left[ \frac{1}{15} \right]^{1/2} \gamma q_4 - \left( \frac{1}{3} \right)^{1/2} \alpha_{134} q_2 / R^6.$$

In these expressions, $\alpha = \alpha_{110} / \sqrt{3}$ designates the isotropic dipole polarizability, $\gamma = \alpha_{112} (\frac{2}{3})^{1/2}$ the dipole polarizability anisotropy, and $q_i$ the static multipole moment of order $l$. The general polarizability components $\alpha_{i11, i2}$ are also defined in Appendix B. The coefficients of $R^{-6}$ appearing on the right-hand sides of Eqs. (20) are well known and are used for a critical test of the asymptotic behavior of the $B_{\lambda_1, \lambda_2, \lambda_3 L}(R)$ components computed here.

Table IV compares the long-range coefficients $B_{\lambda_1, \lambda_2, \lambda_3 L}$ obtained here from Eqs. (19), with the coefficients of $R^{-L-1}$ of Eqs. (20), using accurate values of multipole moments and polarizabilities.\(^{23-26}\) The ab initio coefficients $B^{(4)}_{2023}$ and $B^{(4)}_{2233}$, are seen to be in excellent agreement with these coefficients of the asymptotic expansions, Eqs. (20). Even the small coefficient $B^{(4)}_{4045}$ is in fair agreement with the asymptotic value.\(^{27}\) represents a fit of the anisotropic dispersion contributions, but may also include terms from the dipole-induced dipole mechanism, which also behaves like $R^{-7}$. From the long-range model consideration advanced elsewhere,\(^9,27\) the dispersion dipole should be in the order of $-3 \gamma C_6 R^{-7}$. With $C_6 \approx 12$ a.u., this yields about $-72 R^{-7}$, as compared to the fitted $B^{(7)}_{2023} = -30$.

The dominant component $B^{(4)}_{2023}$ is remarkably well described by its long-range form for all distances considered. Overlap contributions to this term amount to only about $+7\%$ at the collision diameter and increase to

FIG. 1. Significant induced dipole components (solid curves). The dashed curves describe the long-range, quadrupole-induced contributions without overlap.

TABLE III. The dipole fit parameters defined in Eq. (19), with $R_0 = 6$ bohr.

<table>
<thead>
<tr>
<th>Term $c = \lambda_1, \lambda_2, L$</th>
<th>$\beta^{(n)}$ (a.u.)</th>
<th>$a_\epsilon$ (a.u.)</th>
<th>$b_\epsilon$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2023</td>
<td>4</td>
<td>4.529</td>
<td>0.0001916</td>
</tr>
<tr>
<td>2021</td>
<td>7</td>
<td>-29.555</td>
<td>-0.0003271</td>
</tr>
<tr>
<td>2233</td>
<td>4</td>
<td>-0.690</td>
<td>0.0000287</td>
</tr>
<tr>
<td>2211</td>
<td>7</td>
<td>-2.182</td>
<td>-0.0000131</td>
</tr>
<tr>
<td>4045</td>
<td>6</td>
<td>4.420</td>
<td>0.0000435</td>
</tr>
</tbody>
</table>
TABLE IV. Pertinent properties of H₂, and long-range properties of H₂-H₂; the coefficients $B^{\alpha\beta}$ are defined by Eqs. (19) and (20).

<table>
<thead>
<tr>
<th></th>
<th>SCF (a.u.)</th>
<th>CI (a.u.)</th>
<th>Accurateb (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_2$</td>
<td>0.525</td>
<td>0.482</td>
<td>0.485</td>
</tr>
<tr>
<td>$q_4$</td>
<td>0.359</td>
<td>0.333</td>
<td>0.353</td>
</tr>
<tr>
<td>$a_1$</td>
<td>6.773</td>
<td>6.767</td>
<td>6.766</td>
</tr>
<tr>
<td>$a_2$</td>
<td>4.762</td>
<td>4.714</td>
<td>4.752</td>
</tr>
<tr>
<td>$a_{13\sigma}$</td>
<td>0.565</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

H₂-H₂

<table>
<thead>
<tr>
<th></th>
<th>$R^bB^{21}_{102}$</th>
<th>$R^bB^{213}_{102}$</th>
<th>$R^bB^{213}_{102}$</th>
<th>$R^bB^{2145}_{245}$</th>
<th>$R^bB^{2145}_{245}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^bB^{21}_{102}$</td>
<td>4.941b</td>
<td>4.529b</td>
<td>4.552</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^bB^{213}_{102}$</td>
<td>-0.773b</td>
<td>-0.690b</td>
<td>-0.712</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^bB^{245}_{245}$</td>
<td>4.420b</td>
<td>4.420b</td>
<td>4.283</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^bB^{245}_{245}$</td>
<td>0.132</td>
<td>0.132</td>
<td>0.132</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^bB^{245}_{245}$</td>
<td>-0.013</td>
<td>-0.013</td>
<td>-0.013</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*From Refs. 21–24.
*bObtained by fitting the long-range part of the calculated dipole moment function; see Table III.

only 13% at 3.5 bohr. Thus the overlap contributions enhance the spectral intensities by only 10–15%. For $B_{223}(R)$, the overlap contributions are of opposite sign and somewhat larger; see Fig. 1.

The very satisfying agreement between the long-range coefficients $B^{\alpha\beta}$ of the leading components with their accurate asymptotic values (Table IV) demonstrates that our CI wave function separates correctly for large internuclear distances. From this agreement and the degree to which the induction contributions are dominant over all distances, we assess the accuracy of the ab initio calculated dipole moments to be in the order of 1%.

From electron exchange effects, more or less exponentially decaying short-range components $B_{201}(R)$, $B_{221}(R)$, and $B_{231}(R)$, etc., are obtained (Fig. 1). An isotropic overlap term, $\alpha=0$ and $L=1$, which is quite significant in H₂-He, is here absent for reasons of symmetry. Thus overlap terms play a relatively minor role for the H₂-H₂ system.

V. H₂-H₂ INTERACTION POTENTIAL

In order to compute a spectral profile, a potential function must be chosen which models the interaction closely, especially in the region near the collision diameter which is so significant for CIA spectra. The interaction of hydrogen molecules has been a subject of intense research for some time. Schäfer has developed a semiempirical model (S84) that reproduces a number of discriminating measurements and incorporates the anisotropic components obtained from first principles by Meyer. It may be considered one of the most advanced models presently available. However, this work was started many years ago and is based on McConville’s earlier model which was shown to reproduce closely a maximum amount of transport, equilibrium, and scattering data. The differences between Schäfer’s isotropic component and McConville’s potential (which is isotropic) are relatively minor. We simply state here that the former potential model generates spectra which are between 3% (at 300 K) and 6% (at 40 K) more intense than those obtained with the latter; the spectral shapes are virtually identical. Compared with the accuracy of the experimental data (from 5 to 10%), such differences seem barely relevant. In the examples shown below, McConville’s model is used.

The McConville potential shows a narrow scattering resonance in the $l=2$ partial wave at $E_{res}=1.15$ cm⁻¹, with a width of $\Delta E=0.75$ cm⁻¹. Whereas at room temperature the spectroscopic effect of this resonance amounts to only 1–2% of the total CIA intensity (zeroth moment) and less for the higher moments, at low temperatures ($\approx 50$ K) and low frequency shifts ($\approx 70$ cm⁻¹) the resonance contributes $\approx 10\%$ to the absorption. Another resonance at $E_{res} \approx 5$ cm⁻¹ for $l=3$ is about ten times broader. When CIA intensities are computed according to Eq. (10), a careful integration over the free-state energies in the range $E_{res} \pm 5\Delta E$ is essential. Furthermore, the potential features two bound states: $n=0,l=0$ and $n=1,l=1$, at $-2.91$ and $-1.35$ cm⁻¹, respectively. Since for the most important quadrupole induction ($L=3$) the selection rules are $l'-l=m=\pm 1,\pm 3$, with $l=1, l'=0$ being forbidden by the triangular inequalities, we do not have a prominent rotational dimer band. There are, however, discernible bound-free contributions to the spectral intensities that generate observable structures near the centers of the rotational lines that will be discussed below.

We point out that similar dimer energies were computed previously with isotropic model potentials. The energy spacings are, furthermore, in reasonable agreement with the measurements of dimer structures in the rotovibrational (RV) band. We note that dimer levels and dimer emission spectra were recently computed from first principles, taking the anisotropy of the interaction into account.

VI. THEORETICAL SPECTRA

For the significant $\lambda_1\lambda_2\lambda L$ induction components, we have computed values of the various spectral functions at 20 points, over the frequency range from 0 to 1800 cm⁻¹, and for the temperatures of 40, 50, 60, 70, 77.4, 80, 90, 100, 105, 120, 130, 165, 195, 240, 292.2, and 297.5 K. In this work we present mainly those data which can be compared with the existing measurements. In related work we communicate analytical approximations of the computed spectral profiles at the temperatures between 40 and 298 K for easy modeling of radiative transfer in planetary atmospheres which permits the reproduction of the present line-shape computations in seconds.

We compute the zeroth, first, and second spectral moments in two independent ways: by integration of the spectral functions with respect to frequency, Eq. (14), and from the quantum sum formulas. Agreement of the numerical results within 0.3% is observed for the 0223,2023 components, and 1% for the other less important components. This agreement indicates that the line-shape computations are as accurate as numerical tests.
with varying grid widths, etc., have indicated, namely, about 1%.

Spectral moments can also be computed from classical expressions with Wigner-Kirkwood quantum corrections\(^\text{37,4}\) of the order \(O(\hbar^2)\). For the quadrupole-induced 0223 and 2023 components and a temperature of 40 K, such results differ from the exact zeroth, first, and second moments by \(-10\%\), \(-10\%\), and \(+30\%\), respectively. For the leading overlap-induced 0221 and 2021 components, we get similarly \(+14\%\), \(+12\%\), and \(-56\%\). These numbers illustrate the significance of a quantum treatment of the hydrogen pair at low temperatures. At room temperature, the semiclassical and quantum moments differ by a few percent at most.

The effect of accounting for the exchange symmetry \((\gamma_S \neq 0)\) on the spectral moments, and hence on the spectra, is negligible; the extreme variation of \(\gamma_S\) from 0 to 1 modifies the moments \(M_n\) by less than 1% at 40 K, and much less at higher temperatures. It has been previously reported\(^\text{12}\) that exchange symmetry matters at temperatures of less than 10 K. At the temperatures of interest, we may safely neglect symmetry \((\gamma_S = 0)\).

The quadrupole-induced components \(\lambda_1\lambda_2 L = 0223, 2023\) constitute the most important contribution to the spectrum. Figure 2 compares the positive-frequency wings of the various spectral functions, Eq. (10), at a temperature of 77 K. These consist of free-free and bound-free components, the first and third terms to the right of Eq. (10). The dimer structures were suppressed in Fig. 2 but are shown in Fig. 3. The low-frequency end of the spectra of Fig. 2 thus may be considered a low-resolution rendition that may be obtained using a monochromator with an instrumental resolution of about 10 cm\(^{-1}\).

We point out that at 77 K, the positive-frequency wings of the quadrupole-induced components 0223, 2023 have a half-width of about 75 cm\(^{-1}\) (Fig. 2). This relatively small value is typical of the long-range \(R^{-4}\) dependence of the quadrupole induction operator that dominates this interaction. The quadrupole interacting with the anisotropy \(\gamma\) of the polarizability tensor (2233) is seen to be only slightly broader, apparently because it has somewhat more overlap mixed in with the long-range term. However, the pure overlap components 0221,2021 show a half-width about three times greater. The 0445,4045 components are very broad, on account of the high-frequency content of the \(R^{-6}\) dependence characteristic of the hexadecapolar induction. The far wings of the quadrupolar induction term have intensities and logarithmic slopes approaching those of the overlap components, despite the substantial differences at low frequencies. We mention that the red wing (\(\omega < 0\)) of the profile is obtainable from the blue wing by the principle of detailed balance,

\[
g(-\omega; T) = e^{-\hbar\omega/kT}g(\omega; T).
\]  

(21)

This principle holds also for the translational function, \(G_{\lambda_1\lambda_2\lambda L}(\omega; T)\), unless, at the rotational frequencies, special symmetry considerations prevail (dimer spectra below). Where in Fig. 2 two curves are drawn with the same type of line, the upper curve describes the free-free transitions of the collisional pair, and the lower one the bound-free contributions. Asymptotically, at high frequencies, the bound-free contributions amount to only about 1% of the free-free components. At the lower frequencies, however, the bound-free components are much more significant. In fact, the bound-free components which must be superimposed with the free-free components to obtain the spectral function, Eq. (9), affect the shapes of the profiles near the line centers. We note that the quadrupole-induced components 0223, 2023 do not feature a bound-bound spectrum, but the less important overlap components 0221, 2021 do. However, since the absorption due to this overlap component amounts to only a few percent of the total absorption, we neglect here the bound-bound \(l=0\rightarrow 1\) transitions.

While the free-free spectral components vary slowly with frequency, the bound-free contributions show interesting “line” structures at low frequencies which are shown in Fig. 3 for the case of the \(S_0(0)\) line. For a study of such dimer structure near the line centers, the \(l,j\) dependence of the weights \(w(\cdot \cdot \cdot)\) in Eq. (10) must be computed. For processes contributing to the induced \(S_0(0)\) line intensity, at least one of the collisional partners

![FIG. 2. Significant free-free components of the spectral functions of molecular hydrogen pairs at 77 K. For a given set of expansion parameters \(\lambda_1\lambda_2\lambda L\), a different line type is chosen. When two curves of the same type are shown, the upper one represents the free-free, the lower the bound-free contributions; their sum is the total \(VG_{\lambda_1\lambda_2\lambda L}(\omega; T)\). The extreme low-frequency portion of the bound-free contributions with the dimer fine structures is suppressed here.](https://example.com/fig2.png)
must be \textit{para}-H$_2$ in the $j_1=0$ state. The colliding partner, with a probability $P_0$, may also be in the \textit{para}-H$_2$ ($j_2=0$) state. In that case, boson symmetry requires that all odd $l$ values vanish but even $l$'s are enhanced. No symmetry restrictions exist for distinguishable collisional pairs and hence $w = 1 + P_0$ if $l$ is even, and $w = 1 - P_0$ if $l$ is odd. At the temperature of 120 K, $P_0$ amounts to about 0.31. The consideration of the symmetries associated with the induced $S_0(1)$ transitions leads similarly to weights $w$ which are more nearly equal to unity.

In Fig. 3 we notice very small bound-free intensities from 0 to about $\pm 2$ cm$^{-1}$ relative to the H$_2$ rotational transition frequencies. Near about $\pm 2.6$ cm$^{-1}$, peaks that at 120 K amount to roughly 40% of the free-free intensities, are seen. The one to the right arises mainly from transitions of the $l=1$ bound state to the $l'=2$ predissociating state. It is smaller than the one to the left which arises from the inverse $l'=2\rightarrow l=1$ transitions. Their intensity ratio is, therefore, controlled by a factor $(1-P_0)/(1+P_0)$ as described above. The widths of the line structure reflect the lifetime of the predissociating state. One sees another, much broader structure (20 cm$^{-1}$) that peaks near 12 cm$^{-1}$. A smooth roll off begins at frequencies greater than about 30 cm$^{-1}$. At positive frequencies this structure is due to transitions from the other bound state ($l=0$) to the other predissociating state at $l'=3$. These structures are generated by the third term to the right of Eq. (10); the fourth term at positive frequencies is here an empty sum of zero value. We mention that the intensities at negative frequency arise from the inverse transitions of the positive-frequency wing and are obtained from the fourth term in Eq. (10), or by detailed balance, Eq. (21).

Structures similar to these seen in Fig. 3 are obtained for the other induction components (not shown). The anisotropic overlap components 0221,2021 even show a bound-bound transition at 1.6 cm$^{-1}$ which, however, may be hard to detect owing to its narrow width and feebleness. Pressure broadening reduces the line intensity per unit frequency interval. Since in laboratory measurements in hydrogen CIA TR spectra the instrumental widths have generally been roughly 10 cm$^{-1}$ and the pressures in the range of 50 amagat, the structures shown in Fig. 4 were only recently observed in the laboratory with high resolution at low temperature.\textsuperscript{39} It is noteworthy, however, that previously unexplained structures near the $S_0(0)$ and $S_0(1)$ rotational transition frequencies were recorded by the IRIS instrument aboard the Voyager space probes in the upper atmospheres of Jupiter and Saturn.\textsuperscript{30,41} These structures have been explained in terms of the hydrogen dimer fine structure.\textsuperscript{38,42,43} Similar dimer structures are familiar from laboratory measurements of the induced fundamental band of hydrogen.\textsuperscript{35}  

VII. COMPARISON OF THEORY AND MEASUREMENT

For comparison of theory with measurements, we have computed RT spectra of low resolution (=10 cm$^{-1}$ so that no dimer structures are discernible) from 0 to 2250 cm$^{-1}$ at the temperatures for which measurements exist,\textsuperscript{38} Figs. 5–9, using the induced dipole components discussed above. The spectra are given in a semilogarithmic grid so that regions of high and low absorption are rendered with equal weight. The 2211 and the 0445,4045 components are not shown in Figs. 5 and 7 because their intensities are below $10^{-8}$ cm$^{-1}$ amagat$^{-2}$; they are, however, included in the curves marked total. Near the rota-

![FIG. 4. Computed fine structures due to the hydrogen dimer, in the quadrupole-induced (0223,2023) components near the $S_0(0)$ line center at 120 K, the temperature of Jupiter's upper atmosphere. Superimposed with the smooth free-free continuum (long dashes) are structures arising from bound-free (below 354 cm$^{-1}$) and free-bound (above 354 cm$^{-1}$) transitions of the hydrogen pair (short dashes). The convolution of the spectrum with a 4.3-cm$^{-1}$ slit function (approximating the instrumental profile of the Voyager IRIS spectrometer) is also shown (solid line) which looks very similar to the Voyager spectra of Ref. 41.](image-url)
FIG. 5. RT spectrum at 77 K. The dots represent the measurement (Ref. 44). Curves are computed with the ab initio dipole components. Only at high frequencies (> 700 cm⁻¹), the sum of the 0223 and 2023 components (short-dashed curve) differs from the total (solid curve). The 0445, 4045, and 2211 components are also included in the total but are not shown because their intensities amount to less than 10⁻⁷ cm⁻¹ amagat⁻². The theoretical dimer fine structures are suppressed.

FIG. 6. Comparison of measurements of the RT band with theory; an asterisk indicates normal hydrogen. Measurements at 77.4, 130, and 240 K are from Ref. 6; those at 195 and 292 K are from Ref. 44. The theoretical dimer fine structures are suppressed.

FIG. 7. RT spectrum at 297.5 K. Same as in Fig. 5, except the measured spectrum is from Ref. 38.

FIG. 8. Far wing of the RT spectrum at 300 K; measurement from Ref. 46.
(0221, 2021, 0445, 4045) add significantly to the total. At 77 K, Fig. 5, the 2233 component shows five broad structures which from left to right are labeled $S_0(0)$, $S_0(1)$, $2S_0(0)$, $S_0(0)+S_0(1)$, $2S_0(1)$. These are due to simultaneous rotational transitions; the two labels mentioned first stand for combinations $S_0(j_1) + Q_0(j_2)$ involving orientational transitions $Q_0$ of zero frequency shift. Some of these structures at high frequencies should be clearly visible but measurements above 800 cm$^{-1}$ do not exist at this temperature. The agreement of the combined spectral components (solid curve) with a measurement$^{44}$ (dots), Fig. 5, is a satisfactory 5% on the average, with maximal deviations of 12% over a narrow band near 230 cm$^{-1}$. We estimate that the uncertainty of the measurements, which are of that order of magnitude, may fully account for the observed, minor deviations.

Figure 6 compares several other measurements$^6, 38, 44$ of “short” spectra (≤900 cm$^{-1}$) with our computations. Satisfactory agreement, typically better than 10%, is observed at all temperatures, with both equilibrium and “normal” hydrogen. It may be noted that the short spectra at 195 K and room temperature obtained by Dore et al.$^6$, and the spectra in the same region and temperatures obtained by Bachet et al.$^38$ agree to within better than 5%. We conclude, therefore, that the fundamental theory reproduces closely the recent measurements of short spectra within the experimental uncertainty.

Similar spectral components as in Fig. 5 are obtained at 297 K, the highest temperature for which such measurements are available (Fig. 7). With increasing temperature, structures are broader because the duration of the collision is shorter. The structures are also more numerous because more rotational states are populated. The agreement with the measurement$^{38}$ is typically better than 5% except at frequencies above 1500 cm$^{-1}$. At these frequencies, the transmittivity $T$ approached unity at the pressure employed, and the absorption dropped to very low values, to 1% or less of the maximum near 600 cm$^{-1}$. For values of $T$ near unity, the fractional error in the absorption coefficient becomes large$^{45}$ for a fixed uncertainty in $T$, and the measurements are, therefore, less certain. At high frequencies, the deviations of theory from measurement amount to an average of 10% and do not exceed a narrow maximum of 16% near 1600 cm$^{-1}$. For the measurement, uncertainties of such magnitude are to be expected in the far wing as pointed out above. It is, therefore, of interest that a recent measurement$^{46}$ at higher densities of the far wing by Bouanich et al., at frequencies from 1860–2250 cm$^{-1}$ and a temperature of 300 K, indicates somewhat higher absorption, in close agreement with the fundamental theory (Fig. 8).

Another high-frequency spectrum available$^{38}$ was taken at 195 K (Fig. 9). Above 1000 cm$^{-1}$, measurement falls below theory by an average of 10%, with a maximal deviation of −25% near 1200 cm$^{-1}$, but it rises 12% above measurement in a small peak near 1600 cm$^{-1}$. We note that the 195-K measurement deviates from theory discernibly at frequencies from ≈1000 to 1500 cm$^{-1}$ whereas the measurements at the higher temperature follow the theory closely in this range. The peak near 1600 cm$^{-1}$ is believed to be composed of the hexadecapole-induced $U_0(0)$ line, and a superposition of the double transitions $S_0(1) + S_0(3)$ and $2S_0(2)$. The corresponding theoretical profiles, which are also shown, indicate that the $U_0(0)$ transition is rather weak and broad; see the lower curve marked 0445, 4045, Fig. 9, and it compares unfavorably with the structures seen in the measurement (dotted line). The double transitions do indeed produce a feeble structure of roughly the right width (dashed curve marked 2233; see also the solid curve “total,” Fig. 9); the computed structure is also seen in Fig. 7 near 1600 cm$^{-1}$). The measurements, however, appear to be somewhat inconsistent with these computations. According to theory, both spectra should exhibit a small structure near 1600 cm$^{-1}$ of comparable magnitude. However, the 195-K measurement shows a noticeably more pronounced feature compared with that in the 297-K measurement, quite likely because the feature is sharper at 195 K (but still very much broader than the slit width).

Summarizing the comparison of the “long” spectra with the fundamental theory, Figs. 7 and 9, we note inconsistencies at 195 and 297 K in the order of 10 to 15% from 1000 to 1500 cm$^{-1}$. A recent measurement at room temperature$^{46}$ is in agreement with theory at frequencies from 1860 to 2250 cm$^{-1}$. The slight inconsistencies seen in the high-frequency wing of Fig. 7 may, therefore, just reflect the uncertainties of the earlier data.

We give the measured and computed moments $\alpha_1, \gamma_1$, as
function of temperature in Figs. 10 and 11. The solid curves are obtained by integrating the theoretical spectra according to Eqs. (15) and (16). The measurements (dots and circles) agree closely with the theory, well within experimental uncertainties. An estimate of the uncertainties involved may be obtained by noting that the experimental values of $\alpha_1$ and $\gamma_1$ given in Refs. 6 and 44 agree to within 4% or less.

VIII. CONCLUSION

From the \textit{ab initio} induced dipole components and a well-tested isotropic potential, we have computed the CIA RT profiles of hydrogen using an exact wave-mechanical theory. No adjustable parameters are employed. The theoretical profiles and spectral moments are obtained at temperatures where measurements exist; as far as we know, all available measurements are here considered. The comparison of measurement and theory generally shows a very close agreement, typically within the uncertainties of the measurements that are generally of high quality. Small inconsistencies observed at one temperature are not supported by data obtained at another temperature, and some data of the far wing may be affected slightly by ternary interactions not accounted for in a binary theory. In other words, the small inconsistencies mentioned do not cast serious doubt on the theory presented here. The main induction mechanisms, especially the quadrupole-induced 0223,2023 components, are in excellent agreement with observations. Theory can, therefore, be used to reliably predict the spectra at temperatures at which no measurements exist, as is often needed for the modeling of planetary and stellar atmospheres. To facilitate the use of the present data in such applications, in a related paper\textsuperscript{16} we have specified simple analytical functions with parameter sets which allow one to reproduce the exact quantum profiles on computers of small capacity, with rms errors in the 1% range, for temperatures from 40 to 300 K. In this way, quite accurate hydrogen CIA RT spectra can be obtained in seconds without repeating the present quantum calculations. A similar procedure was presented recently for the H$_2$-He CIA RT spectra.\textsuperscript{15}

ACKNOWLEDGMENT

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APPENDIX A: EXCHANGE SYMMETRY

We formulate here the relationships of the exchange symmetry parameter $\gamma_S$ and the para-H$_2$, ortho-H$_2$ densities, $n_p$, $n_o$. We assume low temperatures so that all para-H$_2$ is in the $j=0$, and all ortho-H$_2$ in the $j=1$ state. (Symmetry should not matter at high temperatures.)

For para-H$_2$ pairs, the spins and rotational states are zero, $s_1=s_2=0$ and $j_1=j_2=0$. Accordingly, we have just a single state with a total spin $S=0$ and total angular momentum $J=0$ which are both even. For the Bose symmetry required in this case, only even partial waves occur. The multiplicity equals $(2S+1)(2J+1)=1$.

For ortho-H$_2$ pairs, $s_1=s_2=1$ and $j_1=j_2=1$. So, both for the spin and the rotational wave functions, $|SM_J\rangle$, singlets ($S=0$), triplets ($S=1$), and quintuplets

![Graph 1](attachment:image1.png)

**FIG. 10.** Spectral moment $\gamma_1$ of the RT band: comparison of theory (solid curve) and measurements: closed circles, Ref. 44; open circles, Ref. 38. The measurements of Ref. 6 are close to the above and have not been plotted.

![Graph 2](attachment:image2.png)

**FIG. 11.** Same as Fig. 10, except the RT moment $\alpha_1$ is shown here.
(S = 2) occur of which states with even S, J are even, and odd ones are odd. The overall wave function must be even. Hence even l are associated with those states whose products of |SM⟩ ⟨JM⟩ are even, and odd l if the products are odd. The sum of multiplicities of all even states, S, J = 00, 02, 20, 11, and 22, thus amounts to 45, and those of the odd states, S, J = 01, 10, 12, and 21, amounts to 36. The ratio of even to odd states of ortho-H₂ pairs is, therefore, 5:3.

For a treatment of a mixture of para-H₂ and ortho-H₂, we next compute r_{even}, the fraction of H₂ pairs associated with even l, r_{odd}, the fraction associated with odd l, and r_{no}, the fraction that is void of exchange symmetry (para-H₂-ortho-H₂ pairs), where

\[ r_{even} + r_{odd} + r_{no} = 1. \]  

(A1)

These are related to γ_S according to

\[ 2r_{even} + r_{no} = 1 + \gamma_S, \]  

(A2)

\[ 2r_{odd} + r_{no} = 1 - \gamma_S \]  

(A3)

for even and odd l, respectively. These relationships arise from the fact that the square of the wave function, |Ψ_{total}|^2, is (upon integration over configuration space) the probability of occurrence of that state. Subtracting Eqs. (A3) from (A2), we get at once

\[ \gamma_S = r_{even} - r_{odd}. \]  

(A4)

We note that |γ_S| ≤ 1.

The computation of the fractions r is straightforward. For equilibrium, the para-H₂ and ortho-H₂ densities, n_p, n_o, are obtained from the partition sum of rotational states, but if an excess of para-H₂ is to be accounted for (as is often the case in astrophysics), then the n_p, n_o are input in some form. The number of para-H₂ pairs in the volume V is \( \frac{1}{2} n_p^2 V^2 \) which enters the expression for r_{even} with a multiplicity of unity. The number of ortho-H₂ pairs is \( \frac{1}{2} n_o^2 V^2 \) of which the fraction \( \frac{1}{2} \) enters r_{even}, and the fraction \( \frac{1}{2} \) enters r_{odd}. The number of para-H₂-ortho-H₂ pairs void of exchange symmetry is \( n_p n_o V^2 \), and the total number of H₂-H₂ pairs equals \( \frac{1}{2} (n_p + n_o)^2 V^2 \). Hence, we have

\[ r_{even} = \frac{n_p^2 + \frac{1}{2} n_o^2}{(n_p + n_o)^2}, \]  

(A5)

\[ r_{odd} = \frac{\frac{1}{2} n_o^2}{(n_p + n_o)^2}, \]  

(A6)

\[ r_{no} = \frac{2n_p n_o}{(n_p + n_o)^2}, \]  

(A7)

and, hence,

\[ \gamma_S = \frac{n_p^2 + \frac{1}{2} n_o^2}{(n_p + n_o)^2}. \]  

(A8)

At elevated temperatures, \( \gamma_S \) falls off near zero as a consequence of rotational excitation of the H₂ molecules, and the effect of the summation over many partial waves will further reduce the effects of symmetry.

APPENDIX B: DIPOLE MOMENT INDUCED BY STATIC MULTIPOLE FIELDS

The dipole moment component \( \mu_{\lambda} \) in a frame connected with the intermolecular axis \( \hat{R} \) induced in molecule 2 by electrostatic multipole moments of molecule 1 is obtained from

\[ \mu_{\lambda} = \langle \psi^0 | \hat{Q}_{\lambda}^{\lambda}(2) | \psi^{(1)} \rangle + c.c., \]  

(B1)

where \( \psi^0 = |00\rangle \) and \( \psi^{(1)} = -\sum_i |0_i\rangle \langle 0_i | H^{(1)} |00\rangle E_i^{-1} \) are the unperturbed and perturbed wave functions, respectively, of the molecular pair ground state. The perturbation operator

\[ H^{(1)} = \sum_{\rho \in 1} \sum_{\sigma \in 2} Z_{\rho \sigma} Z_{\sigma \rho} \mu_{\rho \sigma}^{-1} \]  

(B2)

has the well-known two-center expansion \(^{47}\)

\[ H^{(1)} = \sum_{\lambda_1 \lambda_2} \sum_{\mu} \mu_{\lambda_1 \lambda_2}(2) \hat{Q}_{\lambda_1 \lambda_2}^{\lambda_1 \lambda_2}(1) \hat{Q}_{\lambda_2 \lambda_1}^{\lambda_2 \lambda_1}(2)(-1)^\mu, \]  

(B3)

where

\[ b(\lambda_1 \lambda_2 \mu) = \left( \frac{2 \lambda_1 + 2 \lambda_2}{2 \lambda_1} \right)^{1/2} \left( \frac{2 \lambda_1}{2 \lambda_2} \right)^{1/2} \times C[\lambda_1 \lambda_2 (\lambda_1 + \lambda_2); \mu, -\mu, 0] (1)^{\lambda_2 + \mu}. \]  

(B4)

The multipole moment operators,

\[ \hat{Q}_{\lambda}(n) = \left( \frac{4\pi}{2\lambda + 1} \right)^{1/2} \sum_{\rho \in n} Z_{\rho} \hat{r}_\rho Y^\lambda_\rho(n) \]  

(B5)

refer to the frame connected with the intermolecular axis but can be related to the molecular-fixed solid harmonics \( Q^m_\lambda \) by transformation with Wigner rotation matrices,

\[ \hat{Q}_{\lambda}(n) = \sum_m Q^m_\lambda(n) D^{m*}_{\lambda \mu}(n). \]  

(B6)

This leads to

\[ \bar{\mu}_{\lambda} = -2 \sum_{i' \lambda' \lambda_1 \lambda_2 m_1 m_2 \mu} \langle 0 | Q_{\lambda_1 \lambda_2}^{\lambda_1 \lambda_2}(1) | 0 \rangle \langle Q_{\lambda_1 \lambda_2}^{m_1}(2) | 0 \rangle \langle Q_{\lambda_1 \lambda_2}^{m_2}(1) | E_i^{-1} D_{\lambda \mu}^{m_1}(1) D_{\lambda \mu}^{m_2}(2) \rangle \]  

\[ \times D_{\lambda \mu}^{m_1}(2) b(\lambda_1 \lambda_2 \mu)(-1)^\mu R^{-1 - \lambda_1 - \lambda_2}. \]  

(B7)

For a linear molecule, the states \( |i\rangle \) are eigenfunctions of \( \hat{L}_z \) and, therefore, nonvanishing matrix elements require
$$m_1 = 0, m_2 = -v.$$ Then we can use the Clebsch-Gordan series

$$D_{m_2}^{l^*_2, l^*_1} (2) D^*_{-m_2} (2) = \sum_{\lambda_2} D_{\mu + \nu, 0}^{l^*_2} (2) C(\lambda_2 | \lambda_2, m_2 | -m_2, 0) C(\lambda_2 | \lambda_2, \mu, \nu, \nu + \nu),$$

(B8)

and by defining general polarizabilities,

$$a_{\lambda_2 | \lambda_2} = \sum_{m_2} \langle 0 | Q_{\lambda_2}^{m_2} | i \rangle \langle i | Q_{\lambda_2}^{m_2} | 0 \rangle E_i^{-1} C(\lambda_2 | \lambda_2, m_2 | -m_2, 0) (-1)^{l^*_2},$$

(B9)

we obtain

$$\mu_i = -\sum_{\lambda_2 | \lambda_2} a_{\lambda_2 | \lambda_2} q_{\lambda_2} R^{-1 - \lambda - \lambda^*_2} b(\lambda_1 | \lambda_2 \mu | -1) f^{l + \lambda_2} D_{-\mu + \nu, 0}^{l^*_2} (2) C(\lambda_2 | \lambda_2, \mu, \nu, \nu + \nu).$$

(B10)

The product of Clebsch-Gordan coefficients in this expression can be written by means of $6j$ symbols as

$$C(\lambda_2 | \lambda_2, \mu, \nu, \nu + \nu) C(\lambda_2 | \lambda_2, L, \mu, -\mu, 0)$$

$$= \sum_{\lambda_2 \mu} C(\lambda_2 | \lambda_2, \Lambda; -\mu, \nu + m, \nu) C(\Lambda L; 0, \nu) \begin{bmatrix} 2L + 1 \cr 1 \cr \lambda_2 \cr \lambda_2 \cr \lambda_2 \cr \lambda_2 \end{bmatrix}^{1/2} (2L + 1) \begin{bmatrix} 1 \cr \lambda_2 \cr \lambda_2 \cr \lambda_2 \cr \lambda_2 \cr \lambda_2 \end{bmatrix}^{1/2} (2L + 1) \begin{bmatrix} (2L + 1)(2\Lambda + 1) \end{bmatrix}^{1/2} (1),$$

(B11)

with $L = \lambda_1 + \lambda_2$. After replacing $D^{l_0}_{-\mu, 0}(n)$ by $\sqrt{4 \pi/((2L + 1)Y_{\mu}^{l_0}(n))}$, a comparison with the expression, Eq. (5), in the form it takes in the frame connected with the intermolecular axis, i.e., $Y_{\lambda}^{l}(\bar{R}) \Rightarrow [(2L + 1)/2\pi]^{1/2} \delta_{l0}$, leads finally to

$$A_{\lambda_1 \lambda_2 \Lambda L}(R) = [a_{\lambda_1 \lambda_2 \Lambda L} q_{\lambda_2} \alpha(\lambda_1 | \lambda_2) \lambda_2 + (1 - \Lambda) \lambda^*_2 + a_{\lambda_2 \lambda_2 \Lambda L} q_{\lambda_2} \alpha(\lambda_1 | \lambda_2) \lambda_2] R^{-1 - L},$$

(B12)

where

$$a_{\lambda_1 \lambda_2 \Lambda L} = \begin{bmatrix} (2 + \lambda + \Lambda + L)(1 + L - \Lambda)(\Lambda + L + 1)(\Lambda + \lambda_2 - \lambda_1)(1 + \lambda_2 - \lambda^*_2) \end{bmatrix}^{1/2}$$

$$\times \begin{bmatrix} (2 + \lambda_1 + \Lambda + \lambda_2 - \lambda_1)(\Lambda + \lambda_2 - \lambda_1)(1 + \lambda_2 - \lambda^*_2) \end{bmatrix}^{1/2}$$

$$\times \begin{bmatrix} (2 + \lambda_1 + \Lambda + \lambda^*_2)(\lambda_1 + \lambda_2 - \Lambda) \end{bmatrix}^{1/2}.$$  

(B13)

For this result, use has been made of an explicit expression for the special $6j$ symbol in Eq. (B11) given in Ref. 49. For homonuclear molecules, $\lambda_1, \lambda_2$ are even; $\lambda^*_2, L$ are odd. For special cases, one finds special solutions as written out as follows: (i) If $\lambda_2 = 0$, $L = \Lambda + 1$, $\lambda^*_2 = 1$, and

$$A_{\lambda \lambda \Lambda \Lambda L}(R) = \left( \frac{\Lambda + 1}{3} \right)^{1/2} q_{\lambda} \alpha_{\lambda 1 \lambda 2} R^{-\Lambda - 2},$$

(B14)

(ii) If $\lambda_1 = \lambda_2 = \lambda$, $\Lambda = L$, $\lambda^*_2 = \lambda - 1$, and

$$A_{\lambda \lambda \Lambda \Lambda L} = 2 \left( \frac{2(2\Lambda + 1)!}{(\Lambda + 2)(\Lambda - 1)!(\Lambda + 2)!} \right)^{1/2} \times q_{\lambda} \alpha_{\lambda 1 \lambda 2} R^{-\Lambda - 1}.$$  

(B15)

2 J. van Kranendonk, Physica 73, 156 (1974).
46. J. P. Bouanich, C. Brodie, Nguyen-Van-Than, P. Drossart, T. Encrenaz, and E. Lellouch, preliminary data communicated at the second meeting, Laboratory Measurements for Planetary Science, Pasadena, California, 1987 (unpublished). We have been informed that the experimental data have now been finalized and seem to be in even closer agreement with the theory presented here: J. P. Bouanich, C. Brodie, P. Drossart, and E. Lellouch, J. Quant. Spectrosc. Rad. Transfer (to be published).