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Three-body components of collision-induced absorption

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Expressions for the three-body coefficients are derived by virial expansion of the zeroth and first moments of collision-induced spectra. For the ternary supermolecular complexes He-Ar-Ar, He-He-Ar, H_2-He-He, H_2-H_2-He, H_2-H_2-H_2, and H_2-Ar-Ar, these are evaluated numerically from first principles at a few temperatures between 50 and 300 K, using the most dependable induced-dipole and intermolecular potential functions available. Both rototranslational and rotovibrational bands are considered. Only the pairwise-additive contributions to the three-body induced-dipole moments are considered. Quantum corrections of the Wigner-Kirkwood type are given and found to be important. Strong three-body spectral components are predicted at the lower temperatures. The computed three-body spectral moments are compared with available laboratory measurements in the near- and far-infrared regions. At temperatures above 50 K, measured ternary moments are found to be consistently greater than calculated ones, especially at the higher temperatures. The excess may be due to a positive ternary spectral component of collision-induced absorption arising from nonadditive induced-dipole components of molecular triplets.

I. INTRODUCTION

Atoms and molecules like He, Ar, H_2, etc., are infrared inactive because of symmetry. Pairs (or triplets, etc.) of collisionally interacting nonpolar molecules do, however, absorb in the broad vicinity of certain molecular bands in the infrared and microwave regions even if these bands are dipole forbidden in the isolated molecule.[1-4] Collision-induced absorption (CIA) is significant in cool and dense environments, such as planetary[5-7] and certain stellar[8-11] atmospheres, liquids,[12,13] and solids,[14] especially if these are composed of neutral atoms and/or nonpolar molecules. Furthermore, CIA spectra are generated by intermolecular interactions and contain, therefore, information about such interactions. These facts have stimulated extensive CIA studies in various laboratories around the world as available books[15-17] and bibliographies on CIA (Refs. 18 and 19) demonstrate.

In recent years, the CIA spectra of a few simple, binary systems (He-Ar, H_2-He H_2-Ar, H_2-H_2) have been computed from first principles with remarkable precision.[20-25] For the study of the induced-dipole moments, the collisional He-Ar, etc., complexes are treated as a molecule in self-consistent field (SCF) and size-consistent, coupled-electron-pair approximation (CEPA) computations.[26] From these, CIA spectra are computed by numerical procedures with the help of a quantum line-shape formalism, using the *ab initio* induced-dipole functions and a proven interaction potential as input.[21-25] The spectra thus computed were shown to be in close agreement with the best available laboratory measurements of binary CIA spectra. Measurement and theory are consistent with regard to both the shape of spectral profiles and their absolute intensities; these usually agree well within the estimated accuracy of the measurements of typically 10%. Even in the far wings, excellent agreement of computed and observed profiles was found.[25,27] At least for the simpler supermolecular systems mentioned, the binary CIA process appears to be understood accurately and in great, quantitative detail. Binary CIA spectra are observable near the low-density limit where many-body interactions are insignificant. In more practical terms, CIA spectra recorded at densities not exceeding 50 or 100 amagats have often been shown to exhibit an intensity variation proportional to density squared. Such variation is considered convincing evidence that these spectra arise from predominantly binary interactions. (The exceptions are the familiar, more or less striking "intercollisional dips" localized at low frequencies that are due to correlations of dipoles induced in subsequent collisions;[28-30] these involve higher than binary interactions.) It is clear, however, that at high enough densities, besides the intercollisional process, spectral three-body contributions appear that modify the binary profiles to a greater or lesser extent.[31-41]

In this work, we give mathematical expressions for the three-body zeroth and first spectral moments (the third virial spectral coefficients) and evaluate these numerically for the systems He-Ar-Ar, He-He-Ar, H_2-He-He, H_2-H_2-H_2, and H_2-Ar-Ar. Only the pairwise-additive processes are considered here. Quantum corrections of the Wigner-Kirkwood type are specified and found to be important for these light systems, especially at low temperatures. The computational data are presented and, where possible, compared with the few measurements presently available. We will discover that, consistently, measurement suggests greater three-body moments than theory which we take as compelling evidence for the presence of nonadditive induced-dipole components in such spectra.

II. PAIR DIPOLE MOMENTS

The Cartesian components of the pair dipole moment are obtained from first principles as described elsewhere.[21–25] For the purpose of line-shape computations, these data are recast in terms of spherical tensor components $\mu_0=\mu_z$, $\mu_{\pm 1}=\mp(\mu_x \pm i\mu_y)/\sqrt{2}$. For example, for an atom-diatom system like H_2-He, we can write[42–44]

$$\mu_\nu=\frac{4\pi}{\sqrt{3}}\sum_{\lambda,L} A_{\lambda L}(R;r)\sum_{m,m'} C(\lambda L 1;mm'\nu) \times Y_\lambda^m(\hat{\mathbf{r}})Y_L^{m'}(\hat{\mathbf{R}}) , \tag{1}$$

with $\nu=0,\pm 1$. The $C(jj'J;mm'M)$ are Clebsch-Gordan coefficients and the $Y_l^m(\hat{\mathbf{u}})$ are spherical harmonics as usual. $\mathbf{R}$ and $\mathbf{r}$ designate the intermolecular separation and vibrational spacing, respectively; the hat indicates a unit vector. For the systems H_2-He and H_2-Ar, the sum consists of four significant terms[22–24] specified by the combinations of λ and L values 0,1; 2,3; 2,1; and 4,5. Moment computations require the vibrational transition matrix elements

$$B_{\lambda L}(R)=\langle v'J'|A_{\lambda L}(R,r)|vJ\rangle , \tag{2}$$

where v and J are vibrational and rotational states; a prime indicates the final state. The dependence on the rotational state is a weak one and has often been suppressed; see, however, recent work that describes the dependence in some detail.[45,46]

For a complex of three atoms or molecules, the induced-dipole function consists of a combination of pair dipole terms, Eq. (1), plus a nonpairwise-additive component. By neglecting the nonadditive dipole components, we do not imply their insignificance; we merely acknowledge the fact that the irreducible dipole components are not well enough known for our purpose.

III. SPECTRAL MOMENTS

The virial theory of spectral moments is well known[47–51] and will be used here for the computation of the ternary moments. The dipole correlation function

$$C(t)=\frac{4\pi^2}{3\hbar c V}\frac{1}{4\pi\epsilon_0}\langle \boldsymbol{\mu}_{\text{tot}}(0)\cdot\boldsymbol{\mu}_{\text{tot}}(t)\rangle \tag{3}$$

is related to the absorption coefficient $\alpha(\omega)$ in a simple way.[50] In this expression, $\boldsymbol{\mu}_{\text{tot}}$ is the total dipole moment of the system, V is the volume, $\hbar$ is Planck's constant, c is the speed of light, t is time, $\langle\ \rangle$ stands for the thermal average, and ϵ_0 is the permittivity of vacuum. If one uses cgs units as usual, the factor of $1/4\pi\epsilon_0$ equals unity throughout the paper. Spectral moments are defined according to[52]

$$\gamma_n=\left[\frac{-i}{2\pi c}\right]^n \left.\frac{d^n C(t)}{dt^n}\right|_{t=0} . \tag{4}$$

These are related to certain integrals over frequency of the absorption spectra. In what follows, we will be interested only in the lowest two moments, $n=0$ and 1. To avoid cumbersome notation, we shall consider separately three different cases (a), (b), and (c).

(a) Rare-gas mixtures. Let A and B designate the different species of atoms in the mixture. The expansion of the moments in powers of density, up to ternary contributions, may be written as[50]

$$\gamma_n=\rho_A\rho_B(\gamma_n^{(AB)}+\rho_A\gamma_n^{(AAB)}+\rho_B\gamma_n^{(BBA)}) , \tag{5}$$

where ρ_A and ρ_B are the densities in amagat units of the two atomic species and $\gamma_n^{(AB)},\gamma_n^{(AAB)},\gamma_n^{(BBA)}$ are independent of density. Since irreducible three-body contributions to the dipole moment are neglected, terms proportional to ρ_A^3 and ρ_B^3 are missing in Eq. (5).

Comparing Eq. (5) with the results shown in Ref. 51, we see at once that

$$\gamma_0^{(AB)}=\frac{4\pi^2}{3\hbar c}\frac{N_L^2}{4\pi\epsilon_0}\int d^3R\,|\boldsymbol{\mu}(\mathbf{R})|^2 g_0^{(AB)}(R) , \tag{6}$$

$$\gamma_0^{(AAB)}=\gamma_0^{(AAB)'}+\gamma_0^{(AAB)''} , \tag{7}$$

$$\gamma_0^{(AAB)'}=\frac{4\pi^2}{3\hbar c}\frac{N_L^3}{4\pi\epsilon_0}\int d^3R\,|\boldsymbol{\mu}(\mathbf{R})|^2 g_{1A}^{(AB)}(R) , \tag{8}$$

$$\gamma_0^{(AAB)''}=\frac{4\pi^2}{3\hbar c}\frac{N_L^3}{4\pi\epsilon_0} \times\int d^3R\, d^3R'\,\boldsymbol{\mu}(\mathbf{R})\cdot\boldsymbol{\mu}(\mathbf{R}')g_0^{(AAB)}(\mathbf{R},\mathbf{R}') , \tag{9}$$

and similarly for $\gamma_0^{(BBA)}$. Here, $\mathbf{R}$ and $\mathbf{R}'$ are distances between atoms of different kind, $\boldsymbol{\mu}$ is the pair dipole moment, $g_0^{(AB)}$ is the zero-density limit of the pair distribution function, $g_{1A}^{(AB)}$ is the coefficient of ρ_A in the virial expansion of the pair distribution function, $g_0^{(AAB)}$ is the zero-density limit of the triplets distribution function, and $N_L=2.69\times 10^{19}$ $\text{cm}^{-3}\,\text{amagat}^{-1}$ is Loschmidt's number.

For the first moment, we find similarly[51]

$$\gamma_1^{(AB)}=\frac{\pi}{3m_{AB}c^2}\frac{N_L^2}{4\pi\epsilon_0} \times\int d^3R\,[\nabla\boldsymbol{\mu}(\mathbf{R})]:[\nabla\boldsymbol{\mu}(\mathbf{R})]g_0^{(AB)}(R) , \tag{10}$$

$$\gamma_1^{(AAB)}=\gamma_1^{(AAB)'}+\gamma_1^{(AAB)''} , \tag{11}$$

$$\gamma_1^{(AAB)'}=\frac{\pi}{3m_{AB}c^2}\frac{N_L^3}{4\pi\epsilon_0} \times\int d^3R\,[\nabla\boldsymbol{\mu}(\mathbf{R})]:[\nabla\boldsymbol{\mu}(\mathbf{R})]g_{1A}^{(AB)}(R) , \tag{12}$$

$$\gamma_1^{(AAB)''}=\frac{\pi}{3m_B c^2}\frac{N_L^3}{4\pi\epsilon_0} \times\int d^3R\, d^3R'[\nabla\boldsymbol{\mu}(\mathbf{R})]:[\nabla\boldsymbol{\mu}(\mathbf{R}')] \times g_0^{(AAB)}(\mathbf{R},\mathbf{R}') , \tag{13}$$

where m_B is the mass of an atom B and m_{AB} the reduced mass of a pair A and B.

Ternary moments consist of an "intermolecular force" or "finite volume" term (the singly primed terms), and an "interference" or "cancellation" term (the doubly primed terms).[47–49] Actually, a third term arising from the nonadditive ternary dipole components should also be added which we, however, suppress here for lack of detailed information.

We want to express the moments in terms of spherical components of the pair dipole moment. To this end, we write [instead of Eq. (1)]

$$\mu_\nu(\mathbf{R}) = \left[\frac{4\pi}{3}\right]^{1/2} B(R) Y_1^\nu(\hat{\mathbf{R}}) \ . \tag{14}$$

Use of Eq. (14) in Eqs. (6) through (9) yields, with $\boldsymbol{\mu}\cdot\boldsymbol{\mu}' = \sum_\nu \mu_\nu^* \mu_\nu'$,

$$\gamma_0^{(AB)} = \frac{4\pi^2}{3\hbar c}\frac{N_L^2}{4\pi\epsilon_0} 4\pi \int R^2 dR\, [B(R)]^2 g_0^{(AB)}(R) \ , \tag{15}$$

$$\gamma_0^{(AAB)'} = \frac{4\pi^2}{3\hbar c}\frac{N_L^3}{4\pi\epsilon_0} 4\pi \int R^2 dR\, [B(R)]^2 g_{1A}^{(AB)}(R) \ , \tag{16}$$

$$\gamma_0^{(AAB)''} = \frac{4\pi^2}{3\hbar c}\frac{N_L^3}{4\pi\epsilon_0} 8\pi^2 \int_0^\infty R^2 dR \int_0^\infty R'^2 dR' \int_0^\pi \sin\theta\, d\theta\, B(R) B(R') P_1(\cos\theta) g_0^{(AAB)}(R,R',\cos\theta) \ . \tag{17}$$

For this last equation, we have used the relation

$$\sum_\nu Y_1^\nu(\hat{\mathbf{R}}) Y_1^\nu(\hat{\mathbf{R}}') = \frac{3}{4\pi} P_1(\cos\theta) \ , \tag{18}$$

where P_1 is the Legendre polynomial of order 1. Moreover, we have written $g_0^{(AAB)}$ in terms of R, R', and $\cos\theta$, where θ is the angle subtended by $\mathbf{R}$ and $\mathbf{R}'$.

For the first moment, we use the definition

$$(\nabla\boldsymbol{\mu}):(\nabla\boldsymbol{\mu})' = \sum_{\alpha,\nu} (\nabla_\alpha \mu_\nu)^* (\nabla_\alpha \mu_\nu)' \ , \tag{19}$$

where ∇_α is a spherical component of the gradient operator, and apply the gradient formulae[53] to obtain

$$\gamma_1^{(AB)} = \frac{\pi}{3m_{AB}c^2}\frac{N_L^2}{4\pi\epsilon_0} 4\pi \int_0^\infty R^2 dR \left[\left[\frac{dB(R)}{dR}\right]^2 + \frac{2}{R^2}[B(R)]^2 \right] g_0^{(AB)}(R) \ , \tag{20}$$

$$\gamma_1^{(AAB)'} = \frac{\pi}{3m_{AB}c^2}\frac{N_L^3}{4\pi\epsilon_0} 4\pi \int_0^\infty R^2 dR \left[\left[\frac{dB(R)}{dR}\right]^2 + \frac{2}{R^2}[B(R)]^2 \right] g_{1A}^{(AB)}(R) \ , \tag{21}$$

$$\begin{aligned} \gamma_1^{(AAB)''} = {} & \frac{\pi}{3m_B c^2}\frac{N_L^3}{4\pi\epsilon_0} \\ & \times 8\pi^2 \int_0^\infty R^2 dR \int_0^\infty R'^2 dR' \int_0^\pi \sin\theta\, d\theta\, g_0^{(AAB)}(R,R',\cos\theta) \\ & \times \left[\frac{2}{3}\left[\frac{dB(R)}{dR} - \frac{B(R)}{R}\right]\left[\frac{dB(R')}{dR'} - \frac{B(R')}{R'}\right] P_2(\cos\theta) \right. \\ & \left. + \frac{1}{3}\left[\frac{dB(R)}{dR} + 2\frac{B(R)}{R}\right]\left[\frac{dB(R')}{dR'} + 2\frac{B(R')}{R'}\right] P_0 \cos\theta) \right] \ . \end{aligned} \tag{22}$$

An equivalent set of equations derived in the classical approximation for the zeroth and second moments was reported previously.[54] Equations (15) and (20) have been known for some time.[50,51] Our results are rigorous provided quantum distribution functions are input.

We note that in our calculations and in the tables moments M_n are used that are related to the γ_n, according to

$$\gamma_n^{(X)} = \frac{4\pi^2}{3\hbar c}\frac{1}{(2\pi c)^n} M_n^{(X)} \ , \tag{23}$$

where the superscript (X) stands for (AB), (AAB), and (ABB) used in Eq. (5).

(b) Pure hydrogen. In this case, the dipole moment of a molecular pair depends also on the molecular orientations $\hat{\mathbf{r}}_1$ and $\hat{\mathbf{r}}_2$, and vibrational coordinates r_1, r_2. Instead of Eq. (1), we now have

$$\mu_\nu = \frac{(4\pi)^{3/2}}{\sqrt{3}} \sum_{\lambda_1,\lambda_2,\Lambda,L} A_{\lambda_1\lambda_2\Lambda L}(R;r_1,r_2) \sum_{m_1,m_2,m,M} C(\lambda_1\lambda_2\Lambda;m_1m_2m)C(\Lambda L1;mM\nu)Y_{\lambda_1}^{m_1}(\hat{\mathbf{r}}_1)Y_{\lambda_2}^{m_2}(\hat{\mathbf{r}}_2)Y_L^M(\hat{\mathbf{R}}) \; . \tag{24}$$

We will first consider the vibrational matrix elements

$$B_{\lambda_1\lambda_2\Lambda L}(R) = \langle v_1 v_2 | A_{\lambda_1\lambda_2\Lambda L}(R;r_1,r_2) | v_1' v_2' \rangle \tag{25}$$

characteristic of the rotational band in the far infrared, where $v_1 = v_1' = v_2 = v_2' = 0$; the weak rotational dependences of the matrix elements is suppressed here.

It is well known that, in principle, rotational transitions of any order may occur.[47] However, we will assume that the interaction forces are isotropic so that rotations and translations are uncorrelated. In this case, at most, double transitions occur[47] and the correlation function of the total dipole moment can be written as

$$C(t) = \frac{4\pi^2}{3\hbar c}\rho^2 \sum_{\lambda_1,\lambda_2,\Lambda,L} \sum_{j_1,j_1',j_2,j_2'} P(j_1)(2j_1+1)P(j_2)(2j_2+1)$$
$$\times C(j_1\lambda_1 j_1';000)^2 C(j_2\lambda_2 j_2';000)^2 D_{\lambda_1\lambda_2\Lambda L}(t)\exp[it(\omega_{j_1j_1'} + \omega_{j_2j_2'})] \; , \tag{26}$$

where ρ is the density of hydrogen in amagat units; $P(j)$ the probability of occupation of one rotational state with the principal quantum numbers j, m_j; $\omega_{jj'}$ is a rotataional transition frequency; and $D_{\lambda_1\lambda_2\Lambda L}(t)$ is a correlation function which depends only on the motion of the centers of mass of the molecules, but not on their orientation. We next define the moments of $D_{\lambda_1\lambda_2\Lambda L}(t)$ according to

$$M_n^{(c)} = (-i)^n \left. \frac{d^n D_{(c)}(t)}{dt^n} \right|_{t=0} \; , \tag{27}$$

where (c) is short for $\lambda_1\lambda_2\Lambda L$. These moments permit a virial expansion that can be written as

$$M_n^{(c)} = M_n^{(c)}(2) + \rho[M_n^{(c)}(3)' + M_n^{(c)}(3)''] \tag{28}$$

up to ternary contributions; the (2) and (3) mean binary and ternary contributions, respectively.

Expressions for the moments exist that are analogous to Eqs. (6) through (13), except for a replacement of the spherical harmonics Y_1^m by Y_L^M. Since

$$\sum_M [Y_L^M(\hat{\mathbf{R}})]^* Y_L^M(\hat{\mathbf{R}}') = \frac{2L+1}{4\pi} P_L(\cos\theta) \; , \tag{29}$$

with the help of the gradient formula, we compute

$$\sum_M [\nabla B_{(c)}(R) Y_L^M(\hat{\mathbf{R}})]^* [\nabla B_{(c)}(R) Y_L^M(\hat{\mathbf{R}})] \tag{30}$$

and finally arrive at

$$M_0^{(c)}(2) = \tfrac{1}{2} 4\pi N_L^2 \int_0^\infty R^2 dR \frac{1}{4\pi\epsilon_0} [B_c(R)]^2 g_0^{(2)}(R) \; , \tag{31}$$

$$M_0^{(c)}(3)' = \tfrac{1}{2} 4\pi N_L^3 \int_0^\infty R^2 dR \frac{1}{4\pi\epsilon_0} [B_c(R)]^2 g_1^{(2)}(R) \; , \tag{32}$$

$$M_0^{(c)}(3)'' = 8\pi^2 N_L^3 \delta_{\lambda_2 0} \int_0^\infty R^2 dR \int_0^\infty R'^2 dR' \int_0^\pi \sin\theta \, d\theta \, g_0^{(3)}(R,R',\cos\theta) \frac{1}{4\pi\epsilon_0} B_c(R) B_c(R') P_L(\cos\theta) \; , \tag{33}$$

$$M_1^{(c)}(2) = \tfrac{1}{2} \frac{\hbar}{2m_r} 4\pi N_L^2 \int_0^\infty R^2 dR \, g_0^{(2)}(R) \frac{1}{4\pi\epsilon_0} \left[\left[\frac{d}{dR} B_c(R) \right]^2 + \frac{L(L+1)}{R^2} [B_c(R)]^2 \right] \; , \tag{34}$$

$$M_1^{(c)}(3)' = \frac{1}{2} \frac{\hbar}{2m_r} 4\pi N_L^3 \int_0^\infty R^2 dR \, g_1^{(2)}(R) \frac{1}{4\pi\epsilon_0} \left[\left[\frac{d}{dR} B_c(R) \right]^2 + \frac{L(L+1)}{R^2} [B_c(R)]^2 \right] \; , \tag{35}$$

$$M_1^{(e)}(3)''=\frac{\hbar}{2m}8\pi^2N_L^3\delta_{\lambda_2 0}\int_0^\infty R^2dR\int_0^\infty R'^2dR'$$
$$\times\int_0^\pi \sin\theta\, d\theta\, g_0^{(3)}(R,R',\cos\theta)$$
$$\times\frac{1}{4\pi\epsilon_0}\left[\frac{L+1}{2L+1}\left[\frac{d}{dR}B_c(R)-\frac{L}{R}B_c(R)\right]\right.$$
$$\times\left[\frac{d}{dR'}B_c(R')-\frac{L}{R'}B_c(R')\right]P_{L+1}(\cos\theta)$$
$$+\frac{L}{2L+1}\left[\frac{d}{dR}B_c(R)+\frac{L+1}{R}B_c(R)\right]$$
$$\left.\times\left[\frac{d}{dR'}B_c(R')+\frac{L+1}{R'}B_c(R')\right]P_{L-1}(\cos\theta)\right], \tag{36}$$

where $g_0^{(2)}$ is the zero-density limit of the pair distribution function, $g_1^{(2)}$ is the coefficient of ρ of its virial expansion, $g_0^{(3)}(R,R',\cos\theta)$ is the zero-density limit of the triplets distribution function, and m and m_r are the mass of one H_2 molecule and reduced mass of 2 molecules, respectively. With the help of Eq. (27), the γ_0 and γ_1 moments of the rotational band can now be written in terms of the M_n moments,[50]

$$\gamma_0=\frac{4\pi^2}{3\hbar c}\sum_{(c)}M_0^{(c)}, \tag{37}$$

$$\gamma_1=\frac{4\pi^2}{3\hbar c}\sum_{(c)}\left[\frac{1}{2\pi c}M_1^{(c)}\right.$$
$$+\{\nu_{vv'}+[\lambda_1(\lambda_1+1)$$
$$\left.+\lambda_2(\lambda_2+1)]B_{v'-v}\}M_0^{(c)}\right]. \tag{38}$$

In this expression, $B_{v'-v}=\hbar/4\pi cI$ designates the rotational constant (for H_2, $B_0=59.3392$ cm^{-1}), $\nu_{vv'}=0$ for the rotational band $v=v'=0$.

For the fundamental band, the induced-dipole components B_c become the vibrational matrix element,[46] Eq. (25), with $v_1'=1$ instead of 0. Furthermore, each $\lambda_1\lambda_2\Lambda L$ component now occurs twice, once with molecule 1 vibrating and once with 2 vibrating in the final state. This may be taken into account by removing the factors of $\frac{1}{2}$ in Eqs. (31), (32), (34), and (35). Finally, we write the γ_0 and γ_1 moments in the fundamental band by means of the moments M_n with the above prescription, by taking $\nu_{vv'}=4161$ cm^{-1} and $B_1=56$ cm^{-1}.

(c) Hydrogen–rare-gas mixture. The treatment of this case is very similar to the above if one remembers that the induced-dipole component is of the form of Eq. (1). The moment expressions are obtained from Eqs. (31) through (36) by setting $\lambda_2=0$ and removing the factors $\frac{1}{2}$ from Eqs. (31), (32), (34), and (35).

IV. DISTRIBUTION FUNCTIONS

The pair distribution function $g^{(AB)}$ describes the probability that two atoms A,B are separated by the distance R. It is defined as

$$g^{(AB)}(R)=V^2\langle\delta(\mathbf{R}_2-\mathbf{q}_A)\delta(\mathbf{R}_1-\mathbf{q}_B)\rangle, \tag{39}$$

where $\mathbf{R}=\mathbf{R}_2-\mathbf{R}_1$, $R=|\mathbf{R}|$, and the $\mathbf{q}_A$, $\mathbf{q}_B$, designate the laboratory coordinates of the atoms A and B.

The triplets distribution function $g^{(AAB)}(R,R',\cos\theta)$ is proportional to the probability that one atom B and two atoms A form a triangle specified by $R,R',\cos\theta$,

$$g^{(AAB)}(R,R',\cos\theta)=V^3\langle\delta(\mathbf{R}_3-\mathbf{q}_{A'})\delta(\mathbf{R}_2-\mathbf{q}_A)$$
$$\times\delta(\mathbf{R}_1-\mathbf{q}_B)\rangle, \tag{40}$$

with $\mathbf{R}'=\mathbf{R}_3-\mathbf{R}_1$; θ is the angle subtended by the vectors $\mathbf{R}$ and $\mathbf{R}'$. Similar definitions are also valid for $g^{(2)}$ and $g^{(3)}$, the distribution functions of a one-component gas.

We next consider the virial expansions of the distribution functions,[55] specifically

$$g^{(AB)}(R)=g_0^{(AB)}(R)+n_Ag_{1A}^{(AB)}(R)$$
$$+n_Bg_{1B}^{(AB)}(R)+\cdots, \tag{41}$$

$$g^{(AAB)}(R,R',\cos\theta)=g_0^{(AAB)}(R,R',\cos\theta)+\cdots, \tag{42}$$

where the numerical density is given by $n_A=N_L\rho_A$. The $g_0^{(AB)}$, $g_{1A}^{(AB)}$, and $g_0^{(AAB)}$ can be written in terms of the auxiliary functions W, according to

$$g_0^{(AB)}(R)=W_{AB}(\mathbf{R}_1,\mathbf{R}_2), \tag{43}$$

$$g_{1A}^{(AB)}(R)=\int d^3R'[W_{AAB}(\mathbf{R}',\mathbf{R}_2,\mathbf{R}_1)-W_{AB}(\mathbf{R}_2,\mathbf{R}_1)W_{AB}(\mathbf{R}',\mathbf{R}_1)-W_{AB}(\mathbf{R}_2,\mathbf{R}_1)W_{AA}(\mathbf{R}',\mathbf{R}_2)+W_{AB}(\mathbf{R}_2,\mathbf{R}_1)], \tag{44}$$

$$g_0^{(AAB)}(R,R',\cos\theta)=W_{AAB}(\mathbf{R}_3,\mathbf{R}_2,\mathbf{R}_1)\;, \tag{45}$$

with the same notation as in Eq. (40).

The function W_{AB} is defined according to

$$W_{AB}(\mathbf{R}_2,\mathbf{R}_1)=\lambda_A^3\lambda_B^3\mathrm{Tr}[\exp(-\mathcal{H}_{AB}/kT)\delta(\mathbf{R}_2-\mathbf{q}_A)\delta(\mathbf{R}_1-\mathbf{q}_B)]\;, \tag{46}$$

where Tr means trace over the states of a pair of isolated atoms A,B. $\mathcal{H}_{AB}$ is the Hamiltonian of the pair; λ_A and λ_B are the thermal deBroglie wavelengths associated with the two different atoms or molecules A and B.

W_{AA} is given by an expression similar to Eq. (46), with B replaced by another atom of species A. Finally, for the three-body function, we have

$$W_{AAB}(\mathbf{R}_3,\mathbf{R}_2,\mathbf{R}_1)=\lambda_A^6\lambda_B^3\mathrm{Tr}[\exp(-\mathcal{H}_{\mathrm{AAB}}/kT)\delta(\mathbf{R}_3-\mathbf{q}_A)\delta(\mathbf{R}_2-\mathbf{q}_A)\delta(\mathbf{R}_1-\mathbf{q}_B)]\;, \tag{47}$$

where Tr now means the trace over all the states of a system composed of two atoms A and one B. For unmixed gases, we use the same definition with B replaced by another partner of species A, and put the $\rho_B=0$, Eqs. (41) and (43)–(47).

The W functions should be calculated on the basis of quantum mechanics. However, at sufficiently high temperatures and for massive systems, classical or semiclassical expressions in terms of interatomic potential functions $V_{AB}(R)$, etc., are useful. Specifically, in the classical limit, we may write the pair distribution function as

$$W_{AB}(\mathbf{R}_2,\mathbf{R}_1)\to\exp[-V_{AB}(R)/kT]\;, \tag{48}$$

$$W_{AAB}(\mathbf{R}_3,\mathbf{R}_2,\mathbf{R}_1)\to\exp[-V_{AAB}(R,R',\cos\theta)/kT]\;, \tag{49}$$

with V_{AAB} designating the three-body interaction potential; the two members of species A are located at $\mathbf{R}_3$ and $\mathbf{R}_2$, respectively, and B is at $\mathbf{R}_1$. If we neglect the irreducible three-body contributions to the interaction potential, we can write V_{AAB} as a sum of pairwise-additive components as

$$W_{AAB}(\mathbf{R}_3,\mathbf{R}_2,\mathbf{R}_1)\to W_{AB}(R)W_{AB}(R')W_{AA}(R'')\;, \tag{50}$$

where

$$R''=|\mathbf{R}_3-\mathbf{R}_2|=(R^2+R'^2-2RR'\cos\theta)^{1/2}\;.$$

Quantum effects, if small, may be taken into account by expanding the functions W in a power series of $\hbar$. This can be accomplished by using the Wigner-Kirkwood method to calculate the traces which appear in Eqs. (46) and (47). In fact, if $\mathcal{H}^{(n)}$ indicates the Hamiltonian of a system of n atoms whose positions we collectively indicate by $\mathbf{q}^{(n)}$, we have[56,57]

$$\mathrm{Tr}[\exp(-\mathcal{H}^{(n)}/kT)F(\mathbf{q}^{(n)})]=\frac{1}{h^n}\int d^{3n}p\,d^{3n}q\exp[-\mathcal{H}(\mathbf{p}^{(n)},\mathbf{q}^{(n)})/kT][1+\hbar^2\chi(\mathbf{p}^{(n)},\mathbf{q}^{(n)})+O(\hbar^4)]\;, \tag{51}$$

with χ specified in Ref. 57. Using this result, we finally obtain from Eqs. (46) and (47)

$$W_{AB}(\mathbf{R}_2,\mathbf{R}_1)=\exp[-V_{AB}(R)/kT][1+\hbar^2A_{AB}(R)+O(\hbar^2)]\;, \tag{52}$$

$$\begin{aligned}W_{AAB}(\mathbf{R}_3,\mathbf{R}_2,\mathbf{R}_1)=&\exp\{-[V_{AB}(R)+V_{AB}(R')+V_{AA}(R'')]/kT\}\\&\times\{1+\hbar^2[A_{AB}(R)+A_{AB}(R')+A_{AA}(R'')+B_{AAB}(R,R',\cos\theta)]+O(\hbar^4)\}\;,\end{aligned} \tag{53}$$

with

$$A_{AB}(R)=\frac{1}{24m_{AB}(kT)^2}\left[-2\frac{d^2V_{AB}(R)}{dR^2}-\frac{4}{R}\frac{dV_{AB}(R)}{dR}+\frac{1}{kT}\left[\frac{dV_{AB}(R)}{dR}\right]^2\right]\;, \tag{54}$$

$$\begin{aligned}B_{AAB}(R,R',\cos\theta)=\frac{1}{12(kT)^3}&\left[\frac{dV_{AB}(R)}{dR}\frac{dV_{AB}(R')}{dR'}\frac{\cos\theta}{m_B}+\frac{dV_{AB}(R)}{dR}\frac{dV_{AA}(R'')}{dR''}\frac{1}{m_A}\left[\frac{R}{R''}-\frac{R'\cos\theta}{R''}\right]\right.\\&\left.+\frac{dV_{AB}(R')}{dR'}\frac{dV_{AA}(R'')}{dR''}\frac{1}{m_A}\left[\frac{R'}{R''}-\frac{R\cos\theta}{R''}\right]\right]\;,\end{aligned} \tag{55}$$

where R'' is to be thought of as a function of R, R', and $\cos\theta$. From Eqs. (52) and (53), it is seen that W_{AAB} cannot be written as a product of the W functions, as $W_{AB}W_{AB}W_{AA}$. In fact, even in the case of pairwise-additive potentials, we have up to the order $\hbar^2$,

$$\frac{W_{AAB}(R,R',\cos\theta)}{W_{AB}(R)W_{AB}(R')W_{AA}(R'')}=1+\hbar^2B_{AAB}(R,R',\cos\theta)\ . \tag{56}$$

Finally, we rewrite Eq. (44) to include terms to order $\hbar^2$, as

$$\begin{aligned}g_{1A}^{(AB)}(R)=2\pi\exp[-V_{AB}(R)/kT]\int_0^\infty(R')^2dR'\int_0^\pi\sin\theta\,d\theta\\ \times(\exp[-V_{AB}(R')/kT]\exp[-V_{AA}(R'')/kT]\\ \times\{1+\hbar^2[A_{Ab}(R)+A_{Ab}(R')+A_{AA}(R'')+B_{AAB}(R,R',\cos\theta)]\}\\ -\exp[-V_{AB}(R')/kT]\{1+\hbar^2[A_{AB}(R)+A_{AB}(R')]\}\\ -\exp[-V_{AA}(R'')/kT]\{1+\hbar^2[A_{AB}(R)+A_{AA}(R'')]\}\\ +1+\hbar^2A_{AB}(R))\ .\end{aligned} \tag{57}$$

V. RESULTS

A. Helium-argon mixtures

For binary molecular systems of isotropic species such as rare-gas pairs, only a single-induced dipole component exists with λ,L of 0,1; Eqs. (1) and (14). Only dissimilar pairs have a nonvanishing dipole moment. For the He-Ar pair, an *ab initio* induced-dipole surface was previously obtained which, with the help of exact line-shape calculations, was shown to reproduce the measured binary CIA spectra within the accuracy of the measurement if a good intermolecular potential model is used in such calculations.[21] For our computations, we use the "SPFD2" He-Ar (Ref. 58) and the "HFD-C" Ar-Ar (Ref. 59) interaction potentials, along with this induced-dipole function.[21]

Table I shows the results in some detail for four selected temperatures. For each temperature, two lines of results are given: The upper line shows the quantum-corrected results and the lower, starred lines are based on the classical formulas. For the relatively light He-Ar system at low temperatures, quantum corrections are generally significant. Whereas quantum corrections of the binary moments amount to just a few percent, some ternary moments show remarkably strong quantum corrections, from 10 to over 100 %. We note that the correction may even change the sign of M_n'.

The Wigner-Kirkwood corrected results given in starred lines of the table for the lowest temperature may be uncertain, perhaps by some substantial fraction of the quantum correction, and should be considered to be rough estimates.

The binary moments are positive and increasing with temperature as Table I shows in the second and seventh columns. The third, fourth and eighth, ninth columns specify the contributions due to He-Ar-Ar complexes and the fifth, sixth and tenth, eleventh columns give those of the He-He-Ar complexes. We note that strong cancellations of the singly and doubly primed moments are often observed, especially for the zeroth moments, but the M_0' arising from the density-dependent part of the pair distribution function generally dominate unless these terms are near a change of sign. Such a change of sign happens twice, once at temperatures between 45 and 85 K and again at temperatures between 85 and 165 K. The doubly primed three-body moments show much less violent variations with increasing temperature; they are nearly monotonic functions of temperature at the temperatures shown. A comparison of the binary and ternary coefficients shows that the computed density effects are

TABLE I. Various computed moments M_n, with and without Wigner-Kirkwood quantum corrections, for helium-argon mixtures at various temperatures; units of M_0 are 10^{-33} J amagat^{-N} and units of M_1 are 10^{-20} W amagat^{-N}, where $N=2$ for the binary and $N=3$ for the ternary moments. An asterisk means that no Wigner-Kirkwood quantum corrections were made for all entries on that line.

T (K)	$M_0^{(\text{He-Ar})}$	$M_0^{(\text{He-Ar-Ar})'}$	$M_0^{(\text{He-Ar-Ar})''}$	$M_0^{(\text{He-He-Ar})'}$	$M_0^{(\text{He-He-Ar})''}$
45	550	1.220	0.573	0.012	−0.162
*45	520	1.035	0.745	0.013	−0.186
85	680	−0.538	−0.154	0.154	−0.172
*85	658	−0.704	−0.190	0.132	−0.182
165	1 020	0.085	−0.372	0.325	−0.227
*165	1 000	0.066	−0.400	0.306	−0.233
298	1 580	0.818	−0.590	0.535	−0.322
*298	1 570	0.811	−0.611	0.520	−0.326

much stronger at the lower temperatures, especially for the zeroth moment.

B. H_2-Ar-Ar

Tables II and III show the rototranslational spectral moments computed with the "TT3" H_2-Ar (Ref. 60) and the "HFD-C" Ar-Ar interaction potential.[59] The pair dipole surface was shown to describe the measured binary rototranslational spectra closely.[23,61] The second and fifth columns of Table II show the binary zeroth and first spectral moments for the four most important dipole components at a temperature of 195 K, with (upper lines) and without (lower lines) quantum corrections. For the quadrupole-induced component ($\lambda L=23$), quantum corrections are insignificant at 195 K, but for the other components shown, especially for the overlap-induced components ($\lambda L=01$ and 21), these amount to a nonnegligible $\approx 10\%$. For some three-body moments, on the other hand, the quantum corrections are more substantial, Table II. In Table III, only the Wigner-Kirkwood quantum-corrected data are shown.

For the quadrupole-induced component ($\lambda L=23$), ternary zeroth moments $M_0^{(T)}=M_0'+M_0''$ are negative except at the lowest temperature, Table III. Negative zeroth moments are well known from related work with nitrogen[62] and have been observed in several systems where quadrupole induction is significant. The related first moments may be negative or positive, depending on the temperature, and vary rapidly with temperature, even changing signs at a relatively high temperature, somewhere between 195 and 298 K.

At the lowest temperatures, the significance of the three-body moments is again high relative to the binary ones as Table III shows. At the lowest temperature, a density increase of only ≈ 10 amagat will modify the observed moments by roughly 10% of the binary moments. The strong temperature dependence of the three-body moments at low temperature may be quite important for the spectroscopic modeling of planetary atmospheres. It seems to be related to the formation of dimers and, consequently, to monomer-dimer interactions which are three-body processes by our definition. Of course, at 45 K, quantum corrections are so substantial that the numbers quoted must be considered rough estimates only. Nevertheless, the general trend of the temperature dependence is quite clear and the problem must be addressed in future work concerned with planetary atmospheres where temperatures may be as low as 45 K.

C. Hydrogen-helium mixtures

Accurate *ab initio* dipole surfaces for both the rototranslational CIA spectrum in the far infrared[23] and the rotovibrational CIA spectrum in the near infrared[24] have been obtained recently that could be used here to compute the pairwise-additive ternary contributions for both bands. However, to the best of our knowledge, measurements of the density dependence exist only for the fundamental band. For that reason, we present Wigner-Kirkwood corrected computational results only for that band, Table IV.

D. Hydrogen

Accurate *ab initio* dipole surfaces for both the rototranslational CIA spectrum in the far infrared[25] and the rotovibrational CIA spectrum in the near infrared[46] have been obtained recently that could be used here to compute the pairwise-additive ternary contributions for both bands. However, to the best of our knowledge, measurements of the density dependence exist only for the fundamental band. For that reason, we present Wigner-Kirkwood corrected results only for that band, Table V. We note that molecule 1 undergoes the vibrational transition.

Of all gases considered, hydrogen molecules form the lightest complexes. At any given temperature, hydrogen will, therefore, show the strongest quantum corrections obtained in this work.

We note that the intermolecular force effect was previously thought to lead, in general, to positive M_0', but Table V shows that at low temperatures the M_n' are negative. The interference terms M_0'', on the other hand, are generally negative (unless they are zero) and may for the zeroth moments actually be more significant than the force terms.

TABLE I. (*Continued*).

$M_1^{(\text{He-Ar})}$	$M_1^{(\text{He-Ar-Ar})'}$	$M_1^{(\text{He-Ar-Ar})''}$	$M_1^{(\text{He-He-Ar})'}$	$M_1^{(\text{He-He-Ar})''}$
437	1.01	−0.114	0.005	0.016
430	0.878	−0.067	−0.014	0.022
523	−0.422	0.043	0.113	0.016
515	−0.562	0.061	0.098	0.018
747	0.050	0.097	0.232	0.019
742	0.036	0.107	0.220	0.020
1 110	0.557	0.147	0.367	0.026
1 110	0.555	0.155	0.358	0.026

TABLE II. Various computed zeroth and first moments M_n, with and without Wigner-Kirkwood quantum corrections, for a hydrogen-argon mixture at 195 K. Units are 10^{-34} J amagat^{-N} for the zeroth moments, and 10^{-21} W amagat^{-N} for the first moments, with $N=2$ and 3 for binary and ternary moments, respectively. An asterisk means that no Wigner-Kirkwood quantum corrections were made for all entires on that line.

λL	$M_0^{(H_2\text{-Ar})}$	$M_0^{(H_2\text{-Ar-Ar})'}$	$M_0^{(H_2\text{-Ar-Ar})''}$	$M_1^{(H_2\text{-Ar})}$	$M_1^{(H_2\text{-Ar-Ar})'}$	$M_1^{(H_2\text{-Ar-Ar})''}$
23	35 300	−0.62	−37.70	15 200	0.79	−2.50
*23	35 900	−0.34	−38.85	15 330	0.91	−2.55
01	5 010	1.24	−1.42	10 200	2.39	1.78
*01	4 550	1.17	−1.64	9 400	2.31	2.10
21	931	0.19	−0.37	1 420	0.31	0.29
*21	877	0.19	−0.41	1 328	0.30	0.32
45	45	0.006	0.001	60	0.01	0.06
*45	45	0.006	0.001	58	0.01	0.07

VI. COMPARISON WITH MEASUREMENTS

A. Helium-argon mixtures

The density dependence of the helium-argon CIA spectra has been studied at the temperature of 165 K, helium densities from 66 to 130 amagats, and argon densities from 156 to 280 amagats. The ternary moments

$$\gamma_0^{(\text{He-Ar-Ar})}=1.0,\quad \gamma_0^{(\text{He-He-Ar})}=0.7 \tag{58}$$

were reported[35] in units of 10^{-7} cm^{-2} amagat^{-3}. From Table I and Eq. (23), we calculate

$$\gamma_0^{(\text{He-Ar-Ar})}=0.33,\quad \gamma_0^{(\text{He-He-Ar})}=0.56\ , \tag{59}$$

in the same units. Experimental uncertainties were not specified,[35] but the possible errors of a virial analysis of this kind may be very high. In view of presumably large uncertainties, the computed and measured ternary moments may actually be consistent; they are certainly of comparable magnitude and have the correct sign. However, we point out that the measured $\gamma_0^{(3)}$ seem to actually exceed the computed values by some fraction of 10^{-7} cm^{-2} amagats^{-2}.

B. H_2-Ar-Ar

The density variation of the rototranslational CIA spectra of argon gas with a small admixture of hydrogen or deuterium was also studied.[37–39,63] Since there is no induced-dipole component associated with Ar-Ar interactions, the spectroscopically dominant three-body interactions involve one hydrogen molecule and two argon atoms, H_2-Ar-Ar. These spectra consist mainly of quadrupole-induced rotational $S_0(J)$ lines arising from the $\lambda L=23$ component.

CIA spectra obtained at a number of argon densities from 42 to 182 amagats, with 3% hydrogen admixtures,

TABLE III. Temperature variation of the moments of the spectral function for the H_2-Ar-Ar complex; the superscript (12) stands for (H_2-Ar); $M^{(T)}$ is actually the sum of $M^{(122)'}$ and $M^{(122)''}$. Units are 10^{-34} J amagat^{-N} for the zeroth moment and 10^{-21} W amagat^{-N} for the first moments; $N=2$ for the binary moments (third and fifth columns) and $N=3$ for the ternary moments.

λL	T (K)	$M_0^{(12)}$	$M_0^{(T)}$	$M_1^{(12)}$	$M_1^{(T)}$
23	45	53 200	243	21 000	272
	85	39 200	−84.9	15 700	−0.30
	165	35 200	−46.5	14 900	−3.54
	298	37 000	−22.1	16 800	3.15
01	45	4 280	124	9 090	227
	85	3 490	4.61	7 350	10.4
	165	4 470	−0.39	9 160	3.20
	298	7 180	1.23	14 200	8.68
21	45	903	25.2	1 350	31.5
	85	723	0.917	1 080	1.47
	165	851	−0.201	1 290	0.46
	298	1 250	0.036	1 930	1.18
45	45	54.2	1.27	66.0	1.58
	85	41.8	0.072	51.7	0.080
	165	43.3	0.014	56.2	0.013
	298	54.3	0.027	74.8	0.033

TABLE IV. Temperature dependence of the moments of the enhancement spectra of hydrogen-helium mixtures in the fundamental band. The superscript (12) stands for (H_2-He); the term $M_n^{(122)}$ is actually the sum of $M_n^{(H_2\text{-He-He})'}$ and $M_n^{(H_2\text{-He-He})''}$, similar for $M_n^{(112)}$. Unit are 10^{-35} J amagat^{-N} and 10^{-22} W amagat^{-N} for the zeroth and first moments, respectively, with $N=2$ for the binary and $N=3$ for the ternary moments.

T (K)	$M_0^{(12)}$	$M_0^{(122)}$	$M_0^{(112)}$	$M_1^{(12)}$	$M_1^{(122)}$	$M_1^{(112)}$
			$\lambda_L=23$			
45	393	−0.060	−0.018	459	0.087	0.029
85	510	−0.002	−0.036	636	0.177	0.215
165	732	0.072	0.137	1000	0.321	0.486
298	1090	0.016	0.334	1630	0.533	0.861
			$\lambda_L=01$			
45	1750	0.35	−0.543	3670	1.18	−0.447
85	2590	0.58	0.287	5340	2.39	1.93
165	4510	1.02	1.24	9000	4.32	4.89
298	8030	1.71	2.55	15 400	7.14	8.96
			$\lambda L=21$			
45	117	0.024	−0.035	274	0.09	−0.031
85	176	0.042	0.023	411	0.18	0.151
165	320	0.079	0.097	738	0.35	0.410
298	602	0.144	0.212	1370	0.64	0.774
			$\lambda L=45$			
45	5.6	0.0016	−0.0004	16.4	0.005	−0.0022
85	8.2	0.0030	0.0031	24.7	0.009	0.0084
165	14.4	0.0058	0.0080	44.8	0.018	0.024
298	26.2	0.0103	0.0154	84.5	0.034	0.048

show subtle changes of shape and absolute intensity that indicate the presence of many-body effects beyond binary ones. Evaluations in terms of line-shape models and correlation functions[38,39,63] and virial expansions of the line shape[37] have been attempted. In our own (unpublished) analysis of the measurement,[37] the zeroth moment, normalized by the product of densities $\gamma_0/\rho_1\rho_2$, shows a gentle linear decrease with increasing argon density, with a slope that agrees well with theory, Table II,

$$\begin{aligned} M_0^{H_2\text{-Ar-Ar}} &= -3.9 \text{ (experimental)} \\ &= -3.83 \text{ (theoretical)}, \end{aligned} \tag{60}$$

in units of 10^{-33} J amagat^{-3}. The experimental uncertainties should be somewhere between 10% and 25%, but are hard to estimate dependably. The measurement is taken at 195 K.

The first moment, $\gamma_1/\rho_1\rho_2$, on the other hand, seems to indicate some curvature when plotted as function of ρ_2. This is likely to be an artifact; certainly, error bars of only ±10% seem to be sufficient to force a straight line thorugh the data points. If we slightly emphasize the data at low densities, we thus obtain

$$\begin{aligned} M_1^{H_2\text{-Ar-Ar}} &= 20 \text{ (experimental)} \\ &= -1.7 \text{ (theoretical)}, \end{aligned} \tag{61}$$

in units of 10^{-21} W amagat^{-3}. Whereas the ternary zeroth moments agrees closely with theory, the ternary first moments differ widely. We mention, though, that the measured γ_1 is again greater than the theoretical value by about 4×10^{-7} cm^{-2} amagat^{-2}.

C. H_2-He-He

The density dependence of the H_2-He enhancement spectrum in the fundamental band of hydrogen has been measured previously, using a trace of hydrogen in helium of thousands of amagats[32–24]: Ternary moments of

$$\begin{aligned} \gamma_1^{(H_2\text{-He-He})} &= 5.5 \text{ (Refs. 32 and 33)} \\ &= 4.1 \text{ (Ref. 34)}, \end{aligned} \tag{62}$$

in units of 10^{-7} cm^{-2} amagat^{-3}, were reported at room temperature. With the help of Eq. (38), we compute $\gamma_1=3.7$, in the same units. We note that the measurements provide again the greater value.

D. H_2-H_2-H_2

Probably the most substantial measurements of the density dependence of CIA spectra in the fundamental band, at densities from 15 to 400 amagat near the onset of three-body effects, are due to Hunt.[64] He shows a plot of γ_0/ρ^2 as function of the hydrogen density at 6 temperatures, from 40 to 300 K. Especially at the low temperatures, these dependences are well represented by straight lines and thus define the three-body zeroth moments well. No such plots are shown for γ_1/ρ^2 versus ρ, but inferred slopes are reported for both γ_0 and γ_1 in that work as well.

Figures 1 and 2 show the measured three-body moments, γ_0 (squares) and γ_1 (dots), as function of temperature. A visual average of the data presented is sketched (thin lines). For comparison, the calculated theoretical predictions are also plotted (heavy curves). Theory mimics the experimental temperature dependences. Moments are negative at low temperature and increase monotonically with temperature. However, theory and measurements never coincide, the measured values being always the greater values, both for γ_0 and γ_1, for $T > 50$ K.

Errors bars of the experimental data were not specified. However, Hunt provided measurements at two different ortho- to para-H_2 concentration ratios, 3:1 (solid squares and dots) and 1:1 (open squares and circles). According to the theory developed here, variation of this ratio should not substantially affect the results. While symmetry of the interacting H_2 molecules is important at the lowest temperatures (probably lower than 40 K), our semiclassical approach does not distinguish para- and ortho-H_2; we think that the data taken at different ortho-para ratios may in essence reflect the uncertainties of the measurement. We note that earlier works by Chisholm and Welsh[32] and by Hare and Welsh[33] also gave three-body moments $\gamma_1^{(3)}$ of 2 and 1.1×10^{-6} cm^{-2} amagat^{-3}, values that differ from Hunt's measurements roughly by the uncertainties suggested here.

Theory, on the other hand, should be accurate to within roughly 10% as far as the pairwise-additive contributions are concerned. Our theory neglects the slightly different interaction potentials of two H_2 molecules when one is vibrationally excited[24,65,66] which may introduce errors of this magnitude.

It seems, therefore, not unreasonable to assume that the differences observed in Figs. 1 and 2 between theory and measurement are due, in essence, to the pairwise nonadditive three-body contributions. These amount to roughly $\approx 2\times10^{-10}$ cm^{-1} amagat^{-3} for the moment γ_0, and to $\approx 5\times10^{-7}$ cm^{-2} amagat^{-3} for the moment γ_1; the differences increase with temperature as the diverging curves suggest. Such a conclusion is to be taken with the greatest caution, but the difference between theory and measurements shown may be the best evidence yet for the

TABLE V. Temperature dependence of the moments of the CIA spectra of hydrogen in the fundamental band. The superscript (12) stands for (H_2-H_2). Units are 10^{-35} J amagat^{-N} and 10^{-22} W amagat^{-N} for the zeroth and first moments, respectively, with $N=2$ for the binary and $N=3$ for the ternary moments.

T (K)	$M_0^{(12)}$	$M_0^{(122)'}$	$M_0^{(122)''}$	$M_1^{(12)}$	$M_1^{(122)'}$	$M_1^{(122)''}$
			$\lambda_1\lambda_2\Lambda L=0223$			
40	825	−0.508	0	600	−0.343	0
50	847	−0.179	0	622	−0.105	0
60	855	−0.077	0	635	−0.030	0
78	865	0.014	0	650	0.040	0
165	950	0.214	0	760	0.212	0
298	1100	0.338	0	930	0.338	0
			$\lambda_1\lambda_2\Lambda L=2023$			
40	2180	−1.14	−2.76	2255	−0.88	0.129
50	2235	−0.366	−3.40	2307	−0.22	−0.168
60	2263	−0.114	−3.34	2355	0.022	−0.237
78	2320	0.128	−3.07	2460	0.278	−0.254
165	2730	0.750	−2.55	3180	1.08	−0.225
298	3432	1.265	−2.46	4440	1.91	−0.217
			$\lambda_1\lambda_2\Lambda L=0001$			
40	1340	−0.46	−0.103	3600	−1.48	−0.173
50	1323	−0.201	−0.290	3570	−0.63	0.257
60	1350	−0.045	−0.421	3640	−0.165	0.435
78	1445	0.167	−0.583	3885	0.416	0.588
165	2215	0.89	−1.10	5780	2.27	0.927
298	3675	1.84	−1.81	9250	4.52	1.34
			$\lambda_1\lambda_2\Lambda L=0.221$			
40	13.8	−0.007	0	35.9	−0.017	0
50	13.8	−0.004	0	35.6	−0.010	0
60	13.8	−0.002	0	35.6	−0.007	0
78	14.1	−0.001	0	35.8	−0.004	0
165	16.2	0.003	0	39.2	0.002	0
298	20.0	0.005	0	45.6	0.008	0
			$\lambda_1\lambda_2\Lambda L=2021$			
40	238	−0.074	−0.042	670	−0.240	−0.034
50	235	−0.033	−0.067	661	−0.106	0.037
60	240	−0.006	−0.087	673	−0.025	0.068
78	257	0.030	−0.114	720	0.081	0.096
165	399	0.162	−0.205	1090	0.436	0.161
298	675	0.340	−0.335	1790	0.875	0.243

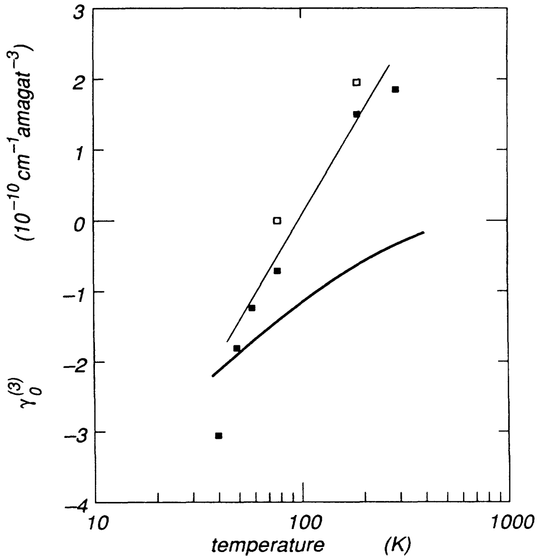

FIG. 1. Comparison of measured three-body γ_0 moments with theory (heavy curve) for hydrogen and the fundamental band; $\gamma_0^{(3)}$: solid and open squares from Ref. 64; the thin line is a visual average through the experimental points.

existence and approximate magnitude of the nonadditive dipole contributions.

VII. RELATED WORK

The theory of ternary processes in CIA was pioneered by van Kranendonk.[49,47] He has pointed out the strong cancellations of the contributions arising from the density-dependent part of the pair distribution function (the "intermolecular force effect") and the destructive interference effects of three-body complexes ("cancellation effect") that lead to a certain feebleness of the theoretical estimates of the ternary effects in CIA spectra.

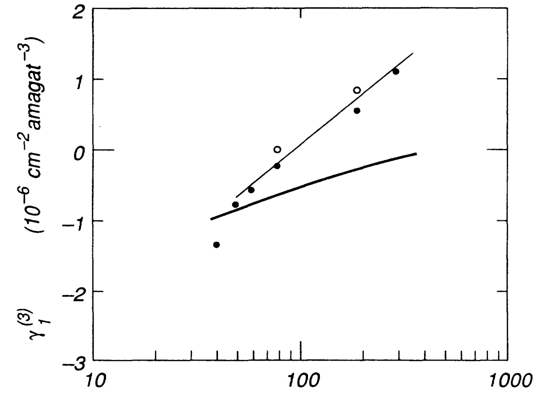

FIG. 2. Comparison of measured three-body γ_1 moments with theory (heavy curve) for hydorgen and the fundamental band; $\gamma_1^{(3)}$: dots and circles form Ref. 64; the thin line is a visual average through the experimental points.

Previous numerical estimates[49] were based on the empirical "exponential plus R^{-4}" (exp-4) induced-dipole model typical of CIA in the fundamental band, and hard-sphere interaction potentials. While the main conclusions are at least qualitatively supported by our present calculations, significant quantitative differences are observed that are related to the use of much improved interaction potentials that are now available; to quantum corrections; and to accurate induced-dipole functions that include significant overlap corrections in the quadrupole-induced terms. It is also affected by our inclusion of the $\lambda_1\lambda_2\Lambda L = 0001$ overlap component (besides the 0221 and 2021 anisotropic overlap components). As a consequence, at 298 K, our three-body moment $\gamma_0^{(3)}$ is negative, -0.34, but the previous value[49] is positive, 0.4, in units of 10^{-10} cm^{-1} amagat^{-3}. If the previous data were plotted in Fig. 1, this difference would not be too striking. According to our results, the force effect is not always positive, nor is it always stronger than the cancellation effect, but for hydrogen near room tempeature, for the main induction components, previous conclusions to that effect[49] are here confirmed.

Freasier and Hamer have previously communicated formulas for the classical zeroth and second moments of CIA spectra of the rare gases;[67] their γ_0 and our M_0 are the same, furthermore, their second moment γ_2 is directly related to our first, M_1,[42,68]

$$M_1 \approx \frac{\hbar}{2kT}\gamma_2 \tag{63}$$

for classical systems; only the $\lambda L = 01$ induced-dipole component is considered and no quantum corrections are given.[67] These authors also compute the moments numerically for the He-Ar-Ar and He-He-Ar complexes using a selection of six widely different empirical[68,69] or theoretical[70] dipole moment functions and simple Lennard-Jones 6-12 potentials as input. Their model 5 (Ref. 68) is closest to the *ab initio* dipole function we use,[21] but most of the other models (as well as the Lennard-Jones interaction potentials[71]) must now be considered obsolete; see the discussions in Refs. 26, 72, and 73. We have performed computations using their induced-dipole model No. 5, along with their Lennard-Jones potentials[67] as input. The results of these calculations are in exact agreement. This fact illustrates the identity of the classical formalisms developed[67] and our $\lambda L = 01$ component without the Wigner-Kirkwood corrections.

Raczynski and Staszewska[74] use Freasier and Hamer's formulas, but with much more refined potentials and a recent *ab initio* dipole surface[75] which, however, should now be replaced by a significantly improved dipole surface.[21] The results are, however, similar to the classical ones shown above for the highest temperature.

A computational study of the density dependence of the rototranslational CIA spectrum of nitrogen, oxygen, and carbon dioxyde was reported by Steele and Birnbaum[62] on the basis of the classical quadrupole induction model. The classical expressions presented here for the case $\lambda L = 23$ are in agreement with that work.

We mention that for the case of collision-induced light scattering of the rare gases ternary components were recently studied.[76–78] Nonadditive contributions of the polarizability of three-body complexes were recently reported.[76] Equations for the zeroth and second classical moments of the anisotropy invariant of the polarizability tensor were reported[78] that are analogous to our Eqs. (31) through (36), with $\lambda_1\lambda_2\Lambda L = 0002$. These expressions were evaluated with the help of the "dipole–induced-dipole" model of the anisotropy invariant. In krypton, an induced anisotropy was observed in excess of the pairwise-additive contributions that was thought to arise form nonadditive polarizability contributions.[76]

VIII. CONCLUSIONS

In recent years, very accurate *ab initio*, binary-induced dipole surfaces became available that permit the computation of CIA spectral profiles and intensities in close agreement with existing measurements of such binary spectra. In the present work, we have used these pair-dipole functions to compute dependable pairwise-additive components of the ternary spectral moments for such systems and conditions for which experimental data are available for comparison.

The comparison (especially with Hunt's data,[64] Figs. 1 and 2) shows that measured ternary moments are consistently greater than calculated ones. Specifically, measured $\gamma_0^{(3)}$ moments exceed the calculated values significantly, roughly by 10^{-10} cm^{-1} amagat^{-3} and the $\gamma_1^{(3)}$ by $\approx 10^{-7}$ cm^{-2} amagat^{-3} in the examples considered above. The excess absorption seems to be increasing with temperature. It is almost certainly related to the nonadditive components of the collision-induced dipoles of molecular triplets that were neglected in our theory.

Very little is known about the irreducible ternary dipole components. An early estimate based on classical electrodynamics, hard-sphere interaction and other simplifying assumptions, suggests very small, *negative* contributions to the zeroth spectral moment,[49] namely, -0.13×10^{-10} cm^{-1} amagat^{-3} in the examples considered above. Various attempts to estimate the effect in unmixed monatomic gases are known[79–82] that were concerned with the asymptotic dipole component but can hardly be expected to account for the excess absorption observed.

In a recent molecular dynamics (MD) study, shapes of intercollisional dips of collision-induced absorption were obtained which are considered a particularly sensitive probe of intermolecular interactions.[83] Using advanced pair potentials and reliable empirical pair-dipole functions, for certain rare-gas mixtures spectral profiles were obtained that differed significantly from what is observed experimentally. This fact was considered compelling evidence for the presence of irreducible three-body forces and dipole moments under such conditions. This independent observation is in qualitative support of our findings. Densities around 1000 amagat were considered in the study.[83]

The classical long-range components of the irreducible ternary induced dipole do probably not generate a significant portion of the effects seen in the figures and the MD study mentioned. Rather, one would think that the nonadditive close-range contributions are more important. Guillot, Mountain, and Birnbaum have developed a "one effective electron model" of the latter, for a first theoretical estimate of the magnitude of the spectroscopic effects.[84,85] For systems like H_2-He-He at liquid state densities, their model suggests significant *enhancement* of the absorption due to overlap induced irreducible dipole components on the basis of MD studies. Our present study shows likewise an enhancement that increases strongly with temperature (figures), which is consistent with an assumption of overlap induction of the irreducible components.

Clearly, more work is required for an accurate description of nonadditive induced-dipole components, and the role of irreducible potential terms, before one can claim in a direct, quantitative way that the excess absorption observed is indeed due to nonadditive dipole components. However, the empirical evidence presented here, as well as other supporting evidence based on theoretical and MD studies[83–85] seems to point unmistakably in that direction. The binary theory has been developed to such a state of perfection that there is hardly any doubt about the correct accounting for the additive dipole components. Since measurement indicates quite consistently greater spectral moments than the pairwise-additive theory predicts, it seems to us a compelling argument for the spectroscopic significance of nonadditive dipole components has been made.

Furthermore, the evidence considered suggests that virial expansions of spectral moments are probably valid procedures at densities of a few hundred amagats.

Wigner-Kirkwood type quantum corrections to order $\hbar^2$ are given for a more realistic evaluation of the ternary moments. It appears that ternary moments are generally associated with much greater quantum corrections than binary moments as the tables illustrate. Quantum corrections are most significant near the repulsive core of the interaction potential and lead to some core penetration. Apparently, for three-body interactions, core penetration is even more significant spectroscopically than for two-body interactions.

Theory suggests that ternary moments may show substantial variations with temperature; even sign changes occur with modest tempeature variations. This simple fact offers intriguing possibilities for experimental sepration of the pairwise-additive and nonadditive three-body effects and, perhaps, for a more critical search for irreducible ternary contributions. A similar conclusion was recently reported for ternary light scattering components.[77]

At low temperatures, the pairwise-additive ternary moments become much stronger relative to the binary components. Experimental studies of the density dependence at low temperatures, besides being of special interest to the planetary specialists, seem to offer an interesting opportunity for probing many-body interactions. Much of the theoretically predicted low-temperature enhancement of ternary components seems to be related to dimer formation; a temperature may be considered "low" if it is comparable to the well depth of the intermolecular interaction potential. For gases like xenon or carbon dioxyde, room temperature may be low enough for a study of that enhancement.

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