Triple Transition $Q_1(j_1) + Q_1(j_2) + Q_1(j_3)$ near 12 466 cm^{-1} in Compressed Hydrogen

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We use the model of the overlap-induced, irreducible, ternary dipole (OITD) component of three interacting H_2 molecules [Phys. Rev. A **49**, 4508 (1994)] to calculate the intensity of the triple Q_1 transition, observed by Reddy, Xiang, and Vaghese [following Letter, Phys. Rev. Lett. **74**, 367 (1995)] in compressed hydrogen gas in absorption near 12 466 cm^{-1}. Such simultaneous transitions in three interacting molecules are thought to arise from irreducible, ternary dipole components. The calculated intensities agree with the measurement within a factor of 2 or 3, which shows once more that the OITD model is capable of describing ternary spectroscopic interaction in remarkable detail.

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One might say that studies of irreducible three-body interactions are at a stage at which it is largely agreed that they are important but reliable theoretical predictions of their magnitude hardly exist, certainly not for the close range of intermolecular interactions (in the repulsive region). Previous work [1,2] deals with the effect of three-body interactions on virial coefficients of high density fluids and on the lattice structure at high densities. The effect on the neutron scattering structure factor has also been considered lately [3], but not much direct evidence of irreducible three-body interactions has yet emerged, because in those cases three-body effects are relatively small corrections to the pairwise contributions.

In this Letter we analyze the effect of irreducible three-body interactions through the interaction-induced dipole moment. In clusters of two or more molecules the interaction-induced dipole moment arises from the same basic mechanisms as the intermolecular forces. Specifically, dipoles are induced, for example, by the polarization of one molecule in the electric multipole field of another molecule, and by momentary rearrangement of electronic charge in the presence of exchange and dispersion forces during collisions [4,5]. It is clear that irreducible three-body contributions to the interaction-induced dipole moment are direct evidence of similar contributions to the intermolecular potential.

The main effect of the interaction-induced dipole moment is that nonpolar gases such as hydrogen absorb infrared radiation in the broad vicinity of the rotovibrational transition frequencies of the interaction molecules, and also at sums and differences thereof [6,7]. We may expand the integrals of the absorption profile, $\gamma = \int A(\omega)\, d\omega$, in powers of the gas density ϱ,

$$\gamma = \gamma^{(1)}\varrho + \gamma^{(2)}\varrho^2 + \gamma^{(3)}\varrho^3 + \cdots \tag{1}$$

(virial expansion). The $\gamma^{(n)}$ represent the n-body contributions [8,9]. In the case of nonpolar gases, the leading coefficient $\gamma^{(1)}$ vanishes. In gases of moderate density, it is thus not too difficult to measure the absorption by binary and ternary molecular complexes separately, making use of the different density dependencies.

Detailed theory and measurements of *binary* induced dipole surfaces [10,11] and their absorption spectra [6,7] exist. Ternary dipoles and their spectra, on the other hand, are less well studied, but are becoming the subject of intense research efforts [12–15]; see also articles by Birnbaum, Moraldi, Zoppi, Weiss, and Frommhold in Ref. [16].

The dipole moment of three interacting molecules consists of a pairwise additive and an irreducible component [9]. We know well the dipole surface of H_2 pairs [17], so that reliable information concerning the pairwise additive dipole components of ternary complexes (H_2-H_2-H_2) exists [14]. We are thus able to calculate the pairwise additive part of the spectral moment $\gamma^{(3)}$. The comparison with Hunt's remarkable measurement [18] of the ternary absorption in the fundamental band of compressed hydrogen shows an absorption *defect* of theory which increases much with temperature, that is compelling evidence for the presence of an irreducible ternary dipole component (which was neglected in that calculation [14]). The striking increase with temperature suggests an irreducible dipole component of the overlap-induced type.

Recent work [15] considers various irreducible ternary dipole mechanisms and models in particular the overlap-induced, irreducible, ternary dipole (OITD) components with the help of Drude's one-effective electron approximation [15,19]. When we combine the OITD model with the pairwise additive dipole component of our previous work [14], theory is capable of reproducing Hunt's measurement reasonably well, including the striking increase of ternary absorption with temperature seen in the measurements [15]. A similar OITD model was also successful in reproducing other many-body spectral features (the

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intercollisional dip [12]). We could also show that several other irreducible components, e.g., the quadrupole-induced dipole-induced dipole (QDID), are not significant and do not mimic the observed temperature variation [15].

To a greater or lesser extent, however, all previous work was affected by the fact that the observed, irreducible three-body effects amounted to a *correction* of the pairwise contributions. As a consequence, the measurements of the irreducible dipole components were indirect, and the uncertainties of the results were often substantial. It is, therefore, noteworthy that recently a more direct measurement of irreducible three-body components of the interaction-induced dipole moment has been reported: an interaction-induced vibrational triple transition near 12 466 cm^{-1} in compressed hydrogen, whose integrated intensity varies as density cubed [20]. The transitions are of the type

$$Q_1(j_1) + Q_1(j_2) + Q_1(j_3), \qquad (2)$$

i.e., a single photon is absorbed, and three interaction H_2 molecules go simultaneously to their lowest excited vibrational states without changing their rotational states. It has long been believed that irreducible ternary dipole components give rise to triple transitions [9,21], but experimental evidence of triple transitions did not exist. The expansion of Eq. (1) is valid also for the triple transitions, but in that case both $\gamma^{(1)}$ and $\gamma^{(2)}$ vanish.

It is thus desirable to determine whether the otherwise very successful theoretical model of the irreducible ternary dipole component [15] is capable of explaining the new measurement [20] as well. The integrated intensity of the triple transition is related to the dipole correlation function at zero time, $V^2\langle \boldsymbol{\mu}(123) \cdot \boldsymbol{\mu}(123) \rangle$. That quantity is here divided by 6 and named M_0. For transitions of the type, Eq. (2), we have

$$\begin{aligned} M_0 = \frac{1}{6} \sum_{\lambda_1\lambda_2\lambda_3\Lambda JLN} I^{LN}_{\lambda_1\lambda_2\lambda_3\Lambda J} \sum_{j_1j_2j_4} n_{j_1} Z^{-1} \exp(-E_{j_1}/kT) \\ \times (2j_1 + 1) C(j_1\lambda_1 j_1; 000)^2 n_{j_2} Z^{-1} \exp(-E_{j_2}/kT) \\ \times (2j_2 + 1) C(j_2\lambda_2 j_2; 000)^2 n_{j_3} Z^{-1} \exp(-E_{j_3}/kT) \\ \times (2j_3 + 1) C(j_3\lambda_3 j_3; 000)^2 . \end{aligned} \qquad (3)$$

M_0 is related to $\gamma^{(3)}$ by

$$\gamma^{(3)} = (4\pi^2/3\hbar c) M_0 . \qquad (4)$$

In this expression $Z = \sum_j n_j(2j + 1)\exp(-E_j/kT)$ is the rotational partition function, n_j are the nuclear weights, $C(\cdots)$ are Clebsch-Gordan coefficients, and E_j are the rotational energies of the H_2 molecule. The statistical averages of the irreducible spherical dipole components $\mathcal{B}$ is given by the triple integral [14]

$$I^{LN}_{\lambda_1\lambda_2\lambda_3\Lambda J} = 8\pi^2 \int\int\int R^2\, dR\, R'^2\, dR' \sin\theta\, d\theta \times g_0^{(3)}(RR'\theta)\, |\mathcal{B}^{LN}_{\lambda_1\lambda_2\lambda_3\Lambda J}(RR'\theta)|^2 . \qquad (5)$$

$g_0^{(3)}(RR'\theta)$ is the three-body distribution function, where R, R', and R'' with

$$R'' = (R^2 + R'^2 - 2RR'\cos\theta)^{1/2}$$

are the separations of molecules 1-2; 1-3, and 2-3, respectively, and θ is the angle subtended by the vectors $\boldsymbol{R}$ and $\boldsymbol{R}'$.

Since the early days of collision-induced absorption, irreducible ternary dipole components were often thought to be due to the QDID mechanism [8,9]: The electric quadrupole field of molecule 1 polarizes the nearby molecule 2, and the electric dipole field of 2 in turn polarizes molecule 3, thus creating an irreducible, ternary dipole in molecule 3. For triple Q_1 transitions, the associated dipole transition matrix element may be written [14]

$$\mathcal{B}^{LN}_{20022} = 3\sqrt{2}\bar{\alpha}^2 \bar{Q}_2 W(2312; 1L) \frac{1}{R''^3} \times \left[-\frac{1}{R^4} X_{LN}(\psi) - \frac{1}{R'^4} Z_{LN}(\theta, \psi) \right], \qquad (6)$$

where $\bar{\alpha}$ and $\bar{Q}^2$ are the vibrational matrix elements for the $v = 0 \longrightarrow v' = 1$ transition of the isotropic polarizability α and the quadrupole moment Q_2 of H_2, respectively; the functions X and Z, etc., are defined elsewhere [15]. The parameter L assumes values of 1 and 3, and since N varies from $-L$ to L, we are looking at ten $\mathcal{B}$ coefficients. But because in general

$$\mathcal{B}^{L-N}_{\lambda_1\lambda_2\lambda_3\Lambda J} = (-1)^N \mathcal{B}^{LN}_{\lambda_1\lambda_2\lambda_3\Lambda J} , \qquad (7)$$

only six integrals I^{LN} are computed for an evaluation of the spectroscopic QDID contributions [14].

In agreement with previous conclusions [15], we will see that the QDID mechanism is much too weak. We therefore consider the two OITD components relevant for triple Q_1 transitions. We see that the dipole component arises as a result of exchange forces. We will use the Drude model, the same model that we have employed for the calculation of ternary moments in the fundamental band that has given satisfactory agreement with experimental results. The charge distribution of each of the three interacting molecules is simulated by a single effective electron with an exponential wave function of the width $2/\beta$, which is to be determined by comparison with known quantities. Usually Gaussian functions are used with Drude's model, because of ease of handling. Exponential functions are, however, more realistic and thus preferred, sacrificing some of the ease of handling in the process.

The width $1/\beta$ of the charge cloud is assumed to be a function of the vibrational coordinate. The electronic wave function of the supermolecular system is the Slater determinant. An induced quantity is obtained by the matrix element of the appropriate operator, which is thus a function of the widths of each exponential wave function and of the vibrational coordinates. If vibrational transitions are involved, as it is the case here, the derivatives with respect to the vibrational coordinates of the interacting molecules are also needed (see [15] for details).

Here we consider two main components for the exchange dipole moment. One arises from the polarization of a molecule in the interaction-induced quadrupole moment created by exchange interaction in two other molecules. The field created by the induced quadrupole moment is simulated by two antiparallel dipoles residing in the two molecules. That contribution is called ADID, for antiparallel dipoles-induced dipole. There is no such contribution from two-body induced dipoles because of symmetry reasons, but higher-order multipoles might be created, though they are expected to give negligible contributions. Specifically, the ADID components are

$$\mathcal{B}^{10}_{00000} = \frac{Q(R)\bar{\alpha}}{2R}\left[\frac{1-3(\cos\theta)^2}{R'^3} - \frac{1-3(\cos\psi)^2}{R''^3}\right] - \frac{Q(R')\bar{\alpha}}{2R'}\left[\frac{2\cos\theta}{R^3} + \frac{\cos\theta - 3\cos(\psi-\theta)\cos\psi}{R''^3}\right] - \frac{Q(R'')\bar{\alpha}}{2R''}\left[\frac{2\cos\psi}{R^3} + \frac{\cos\psi - 3\cos(\psi-\theta)\cos\theta}{R'^3}\right], \tag{8}$$

$$\mathcal{B}^{11}_{00000} = \frac{3Q(R)\bar{\alpha}}{2\sqrt{2}R}\left[\frac{\sin\theta\cos\theta}{R'^3} - \frac{\sin\psi\cos\psi}{R''^3}\right] - \frac{Q(R')\bar{\alpha}}{2\sqrt{2}R'}\left[\frac{\sin\theta}{R^3} - \frac{\sin\theta - 3\cos(\psi-\theta)\sin\psi}{R''^3}\right] - \frac{Q(R'')\bar{\alpha}}{2\sqrt{2}R''}\left[\frac{\sin\psi}{R^3} - \frac{\sin\psi - 3\cos(\psi-\theta)\sin\theta}{R'^3}\right], \tag{9}$$

which with Eq. (7) gives three $\mathcal{B}$ terms so that only two integrals I^{LN} must be computed. The exchange-induced quadrupole moments $Q(R)$ are computed with the help of the Drude one-effective electron approximation, with the result

$$Q(R) = -\frac{4}{5}eR^2\left(\frac{\hbar}{2M\omega_0}\right)\left(\frac{\beta'}{\beta}\right)^2 \exp(-\beta R)\left(1 + x + \frac{8}{21}x^2 + \frac{1}{21}x^3 + \frac{11}{32}\frac{x^4}{315} + \frac{197}{128}\frac{x^5}{315} + \frac{x^6}{1260}\right). \tag{10}$$

We introduce the abbreviations $x = \beta R$, $x' = \beta R'$, and $x'' = \beta R''$, where $\beta = 2.446$ a.u. is the reciprocal range parameter of the exponential wave function and $\beta' = -3.856$ a.u. is its derivative with respect to the bond distance; see Ref. [15] for details. Finally we have also a purely exchange (OVID) term, arising when all three molecules are close to each other at distances comparable to the single electron width.

In the case of triple Q_1 transitions, the OVID expressions are

$$\begin{aligned} \mathcal{B}^{10}_{00000} &= \frac{9e}{2}\left(\frac{\beta'}{\beta}\right)^3\left(\frac{\hbar}{2M\omega_0}\right)^{3/2} \\ &\quad\times \exp\left(-\frac{x+x'+x''}{2}\right) f^{10}_{00000}(x,x',x''), \\ \mathcal{B}^{11}_{00000} &= \frac{9e}{2\sqrt{2}}\left(\frac{\beta'}{\beta}\right)^3\left(\frac{\hbar}{2M\omega_0}\right)^{3/2} \\ &\quad\times \exp\left(-\frac{x+x'+x''}{2}\right) f^{11}_{00000}(x,x',x''), \end{aligned} \tag{11}$$

with f functions going to zero when the separations go to zero. Details of these calculations will be given in a forthcoming paper.

We write the coefficient of density cube, ϱ^3, of the integrated absorption intensity for transitions of the type (2) as

$$M_0^{j_1j_2j_3} = \frac{1}{6}P(j_1,j_2,j_3) \times \left\{3C(j_1 2_{j_1};000)^2 \sum_{LN} I^{LN}_{20022} + \sum_{N} I^{1N}_{00000}\right\}, \tag{12}$$

where $P(j_1,j_2,j_3)$ is the probability that three molecules are in the rotational states j_1, j_2, and j_3, without specifying which of the molecules is in a particular rotational state. At the lowest temperatures the only rotational states populated are those with $j = 0$ and 1. There are four of these states that can be labeled according to j as $(j_1, j_2 j_3) = (111, 110, 100, 000)$. The four $3Q_1$ transitions just mentioned appear at the frequencies of 12 465.8, 12 471.7, 12 477.6, and 12 483.5 cm^{-1}, respectively. Owing to the short duration of ternary collisions, these lines are very diffuse and cannot be resolved spectroscopically. We compare, therefore, the observed integrated intensity with the sum of the above four moments M_0, Eq. (12). The first one of the two sums in Eq. (12) consists of the ten QDID terms, and the second sum is over a total of six ADID and OVID terms.

TABLE I. Results.

	OITD	QITD	Total	Calc.	Meast.[a]
T	$\sum_N I^{1N}_{00000}$	$\sum_{LN} I^{LN}_{20022}$	$\sum_j M_0$	$\gamma^{(3)}(3Q_1)$	
(K)	(10^{-72}erg cm^{6}amagat^{-1})			(10^{-14} cm^{-1} amagat^{-3})	
77	265	7.4	44.4	1.3	0.71
125	311	7.9	48.8	1.6	
195	403	9.0	51.3	2.0	0.88[b]
300	562	10.9	46.2	2.8	0.88[c]

[a] From [20].

[b] At 201 K.

[c] At 298 K.

At the higher temperatures states of $j > 1$ are also populated. We note, however, that the QDID terms contribute only a few percent of the total. If the QDID terms are neglected, the sum over all rotational states can be performed explicitly so that

$$M_0 = \frac{1}{6} \sum_N I^{1N}_{00000} \,. \tag{13}$$

The ternary distribution function $g_0^{(3)}$ is computed from a classical expression with Wigner-Kirkwood quantum corrections of order $\hbar^2$ [14].

Table I shows the results of our computations. The spatial averages I^{1N}_{00000} of the combined ADID and OVID components (column 2) are 1 or 2 orders of magnitude stronger than the $\sum I^{LN}_{20022}$ quadrupole-induced dipole-induced dipole (QDID) components (column 3). The sums of the four moments M_0 of Eq. (12) are given in column 4. For comparison with the measurement [20], these must be multiplied by $(4\pi^2/3\hbar c)N_L^2$ [14,15] to get the spectral integrals (column 5).

The results of the measurement [20] were reported as integrals of the absorption coefficient $\alpha(\nu;T)$, over density cubed, over frequency (in cm^{-1} units),

$$\alpha^{(3)} = \int \alpha(\nu;T)d\nu/\varrho^3 \,, \tag{14}$$

in units of cm^{-2} amagat^{-3}. We have computed here a slightly different expression,

$$\gamma^{(3)} = \int \alpha(\omega;T)d\omega/\omega\,\varrho^3 \,, \tag{15}$$

in units of cm^{-1} amagat^{-3}. Because of the small frequency band involved, from roughly 12 300 to 12 700 cm^{-1}, we may convert the measured quantity $\alpha^{(3)}$ to the computed quantity $\gamma^{(3)}$ by dividing by the mean frequency, 12 500 cm^{-1}. This is how the last column of Table I was obtained from the measurement.

In other words, as the comparison of the last two columns of Table I shows, within the acceptable factor of 2 or 3, observed and calculated intensities of the $3Q_1$ transition are consistent. The model of the OITD component [15], which was heretofore shown to be successful to describe the intercollisional dip [12] and the ternary absorption moment of the H_2 fundamental band [15], has once more shown that it is capable of explaining the available, relevant measurements. Additional evidence for the significance of the overlap-induced, ternary irreducible dipole component is thus provided.

[1] F.H. Ree and C.F. Bender, Phys. Rev. Lett. **32**, 85 (1974).
[2] P. Loubeyre, Phys. Rev. Lett. **58**, 1857 (1987).
[3] M. Tau, L. Reatto, R. Magli, P.A. Egelstaff, and F. Barocchi, J. Phys. Condens. Matter **1**, 7131 (1989).
[4] A.D. Buckingham, in *Propriétés Optiques et Acoustiques des Fluides Comprimés et Actions Intermoléculaires Colloques International du C.N.R.S.* (C.N.R.S., Paris, 1959), Vol. 77, p. 57.
[5] J. van Kranendonk, Physica (Utrecht) **24**, 347 (1958).
[6] H.L. Welsh, *Spectroscopy,* edited by D.A. Ramsey, MTP International Review of Science, Physical Chemistry, Series I (Butterworths, London, 1972), Vol. III, p. 33.
[7] L. Frommhold, *Collision-Induced Absorption in Gases* (Cambridge University Press, Cambridge, 1993).
[8] J. van Kranendonk, Physica (Utrecht) **23**, 825 (1957).
[9] J. van Kranendonk, Physica (Utrecht) **25**, 337 (1959).
[10] W. Meyer, in *Phenomena Induced by Intermolecular Interactions*, edited by G. Birnbaum (Plenum, New York, 1985), p. 29.
[11] W. Meyer and L. Frommhold, in *Induced Spectroscopy: Advances and Applications*, Ref. [16].
[12] B. Guillot, R.D. Mountain, and G. Birnbaum, J. Chem. Phys. **90**, 650 (1989).
[13] B. Guillot, J. Chem. Phys. **91**, 3456 (1989).
[14] M. Moraldi and L. Frommhold, Phys. Rev. A **40**, 6260 (1989).
[15] M. Moraldi and L. Frommhold, Phys. Rev. A **49**, 4508 (1994).
[16] *Induced Spectroscopy: Advances and Applications*, edited by G.C. Tabisz (Kluwer, Amsterdam, 1994).
[17] W. Meyer, A. Borysow, and L. Frommhold, Phys. Rev. A **40**, 6931 (1989).
[18] J.L. Hunt, Ph.D. thesis, University of Toronto, 1959.
[19] B. Guillot, R.D. Mountain, and G. Birnbaum, Mol. Phys. **64**, 747 (1988).
[20] S.P. Reddy, Fan Xiang, and G. Varghese, following Letter, Phys. Rev. Lett. **74**, 367 (1995).
[21] J.D. Poll, in *Spectral Line Shapes*, edited by L. Frommhold and J.W. Keto Vol. 6, p. 473 (AIP, New York, 1990).