

Modelling the anisotropy of the potential in the dynamics of solid nitrogen

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1990 J. Phys.: Condens. Matter 2 8015

(<http://iopscience.iop.org/0953-8984/2/40/003>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 11/05/2010 at 06:54

Please note that [terms and conditions apply](#).

Modelling the anisotropy of the potential in the dynamics of solid nitrogen

T H M van den Berg, M M G Bongers and A van der Avoird

Institute of Theoretical Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Received 18 May 1990

Abstract. Using a spherical expansion of an *ab initio* N_2 – N_2 potential, we have calculated harmonic lattice vibration frequencies for solid α - and γ -nitrogen, in good agreement with experiment and time-dependent Hartree calculations. Previous dynamics calculations with an (isotropic) atom–atom model fitted to the same *ab initio* potential yielded libron frequencies that were considerably too high. We conclude, therefore, that the atom–atom model does not do justice to the accurate anisotropy of intermolecular potentials found by *ab initio* calculations. The upward shifts of the lattice frequencies caused by the anharmonicity in the potential agree well with the results from Green function calculations based on model potentials.

1. Introduction

Solid nitrogen, as one of the simplest molecular crystals, is used as a testing ground for modelling intermolecular potentials [1] and for lattice dynamics methods [2]. A large body of experimental data has been collected [3] and many calculations have been performed [1] especially on the low-temperature α -phase and the higher-pressure γ -phase. In these ordered solids the molecules perform oscillations around their equilibrium positions and orientations. The angular oscillations are determined by the anisotropy of the intermolecular potential. This anisotropy can be modelled in different ways: implicitly, by the use of an atom–atom potential, or explicitly, by a spherical expansion of the potential, which is a generalization of the electrostatic multipole expansion [4]. In practice [5], atom–atom potentials are mostly understood to imply isotropic interactions between atoms. This restriction leads to an approximation of the anisotropy in the intermolecular potential. Some authors [6–10] have proposed anisotropic atom–atom interactions. If these are chosen sufficiently flexible, they may reproduce the exact anisotropy of the intermolecular potential in a rather quickly converging form [8–10]. The use of such isotropic or anisotropic atom–atom potentials is especially attractive for larger molecules.

Standard harmonic lattice dynamics calculations on α - and γ -nitrogen have been performed using either *ab initio* [11] or semi-empirical N_2 – N_2 potentials [1]. An *ab initio* potential, obtained from quantum chemical calculations [12], has not been fitted to experimental (solid state) data and, therefore, is not dependent on the approximations made in the dynamics model. Such a potential can also be used to calculate gas state [13] or liquid state [14] properties of nitrogen and it yields satisfactory results,

in general. Harmonic lattice dynamics calculations, using the *ab initio* N_2 - N_2 potential of Berns and Van der Avoird [15], resulted in translational phonon frequencies in good agreement with experiment [11]. The calculated libron frequencies, corresponding with collective angular oscillations, came out about 30% too high, but this was believed to be due mainly to the failure of the dynamical model. Inclusion of potential anharmonicities and zero-point motion effects via the self-consistent phonon method [16] did not improve the libron frequencies significantly [11].

In order to describe strongly anharmonic motions, Briels, Jansen and Van der Avoird [17, 18] developed a quantum mechanical lattice dynamics method, based on the time-dependent Hartree (TDH) formalism, in which the rotational molecular wave functions are expanded in a basis of free rotor functions. Also anharmonic potential terms up to fourth order inclusive in the translational displacements are taken into account. Mean-field calculations showed that the single-particle rotational states are rather localized and that the corresponding set of energy levels resembles the spectrum of a two-dimensional harmonic oscillator [17]. Surprisingly, the TDH calculations yielded libron frequencies in good agreement with experiment, whereas the (quasi-)harmonic models failed.

The discrepancy between the two lattice dynamics methods described above might be caused by the use of different analytical representations of the intermolecular potential. In the harmonic model, the force constants were calculated as second derivatives of an exp-6-1 isotropic atom-atom potential model [11], which was fitted to the *ab initio* N_2 - N_2 potential surface. The inaccuracies in the fits of the individual exchange, dispersion and electrostatic contributions are less than 10% [15]. The resulting inaccuracy in the overall potential, for instance, in the Van der Waals well depth is larger, however. The TDH calculations, on the other hand, used a spherical expansion [17] of the potential, which represents its anisotropy exactly.

In the following, we present analytical formulas required for the evaluation of the force constants of a spherical potential expansion. Using these force constants, harmonic lattice vibration frequencies are calculated for α - and γ -nitrogen, which will be compared with atom-atom results, TDH and experiment. Thus, we can explicitly separate the effects of approximations made in the anisotropy of the intermolecular potential and the effects of anharmonicity on the calculated phonon and libron frequencies.

2. Force constants from a spherically expanded potential

The anisotropy in the interaction between two linear molecules p and p' is represented explicitly by the following spherical expansion [12]

$$V_{pp'}(\omega_p, \omega_{p'}, \mathbf{R}_{pp'}) = \sum_l \Phi_l(R_{pp'}) \sum_{\mathbf{m}} \begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{pmatrix} C_{m_1}^{(l_1)}(\omega_p) C_{m_2}^{(l_2)}(\omega_{p'}) C_m^{(l)}(\Omega_{pp'}) \quad (1)$$

which contains a summation over $l = (l_1, l_2, l)$ and $\mathbf{m} = (m_1, m_2, m)$. The vector $\mathbf{R}_{pp'} = \mathbf{R}_{p'} - \mathbf{R}_p$ connects the centres of mass of the molecules at positions \mathbf{R}_p and $\mathbf{R}_{p'}$; $\Omega_{pp'} = (\vartheta_{pp'}, \varphi_{pp'})$ denotes the polar angles of $\mathbf{R}_{pp'}$ with respect to the global crystal frame. Further, $\omega_p = (\vartheta_p, \varphi_p)$ describes the orientation of the molecular axis also with respect to the global frame. In (1), $C_m^{(l)}$ is a Racah spherical harmonic function [19]

and the symbol following the second summation sign is a Wigner $3j$ coefficient. The distance-dependent expansion coefficients $\Phi_i(R_{pp'})$ can be obtained from *ab initio* calculations [15,20]. They contain electrostatic ($R_{pp'}^{-l_1-l_2-1}$), dispersion ($R_{pp'}^{-n}$, $n = 6, 8, 10$) and (exponential) exchange contributions.

In harmonic lattice dynamics calculations, one needs the second derivatives of the total crystal potential with respect to the external molecular coordinates

$$Q_{p\lambda} = \begin{cases} R_{p\tau} & (\tau = x, y, z) \\ \omega_{p\rho} & (\rho = \vartheta, \varphi) \end{cases} \quad (2)$$

If the crystal potential is assumed to be a sum of pairwise interactions the force constants are given by

$$F_{pp'}^{\lambda\lambda'} = \frac{\partial^2 V_{pp'}}{\partial Q_{p\lambda} \partial Q_{p'\lambda'}} \quad (p' \neq p)$$

$$F_{pp}^{\lambda\lambda'} = \sum_{p' \neq p} \frac{\partial^2 V_{pp'}}{\partial Q_{p\lambda} \partial Q_{p'\lambda'}} \quad (3)$$

The self-term $F_{pp}^{\lambda\lambda'}$ contains a lattice sum that can be replaced, using translational and rotational invariance conditions [21–23], by an alternative expression in terms of intermolecular couplings $F_{pp'}^{\lambda\lambda'}$ with $p' \neq p$.

The rotational force constants contain derivatives of Racah harmonic functions $C_m^{(l)}$ with respect to molecular angles φ that can be easily evaluated using [19]

$$\frac{\partial^n}{\partial \varphi^n} C_m^{(l)}(\vartheta, \varphi) = (im)^n C_m^{(l)}(\vartheta, \varphi). \quad (4)$$

The first derivative of a Racah harmonic with respect to ϑ is also fairly standard and obeys [24]

$$\sin \vartheta \frac{\partial}{\partial \vartheta} C_m^{(l)}(\vartheta, \varphi) = -(l+1) \cos \vartheta C_m^{(l)}(\vartheta, \varphi) + [(l+1)^2 - m^2]^{1/2} C_m^{(l+1)}(\vartheta, \varphi). \quad (5)$$

Applying (5) twice and using recurrence relations for the Racah harmonics [24] we find

$$\begin{aligned} \sin^2 \vartheta \frac{\partial^2}{\partial \vartheta^2} C_m^{(l)}(\vartheta, \varphi) &= [(l+1) \cos^2 \vartheta + m^2 - l(l+1) \sin^2 \vartheta] C_m^{(l)}(\vartheta, \varphi) \\ &\quad - [(l+1)^2 - m^2]^{1/2} \cos \vartheta C_m^{(l+1)}(\vartheta, \varphi). \end{aligned} \quad (6)$$

One has to be careful, however, if $\vartheta = 0$ or π because [24]

$$\lim_{\vartheta \rightarrow n\pi} \frac{\partial}{\partial \vartheta} C_m^{(l)}(\vartheta, \varphi) = \frac{1}{2} (-1)^{nl} (\delta_{m-1} e^{-i\varphi} - \delta_{m+1} e^{i\varphi}) [l(l+1)]^{1/2} \quad (n = 0, 1) \quad (7)$$

which is not uniquely defined. A similar problem occurs for the second derivative with respect to ϑ if $m = -2, 0$ or 2 . Therefore, one should avoid, by a convenient choice of

the global frame, the possibility that at equilibrium the molecules are oriented parallel to the z axis.

In order to evaluate the translational force constants it is convenient to use spherical tensor coordinates R_μ defined by [19]

$$R_{+1} = -\frac{1}{\sqrt{2}}(R_x + iR_y) \quad R_0 = R_z \quad R_{-1} = \frac{1}{\sqrt{2}}(R_x - iR_y). \quad (8)$$

The position-dependent part of the spherical expansion of (1) is a function of the intermolecular vector $\mathbf{R}_{pp'}$. Therefore, all derivatives with respect to individual molecular coordinates $R_{p\mu}$ and $R_{p'\mu}$ can be expressed in derivatives with respect to intermolecular components $R_{pp'\mu}$ according to

$$\frac{\partial}{\partial R_{p\mu}} = -\frac{\partial}{\partial R_{p'\mu}} = -\frac{\partial}{\partial R_{pp'\mu}}. \quad (9)$$

Using the spherical gradient formula of [18] and [19], it follows that

$$\frac{\partial}{\partial R_\mu} \Phi_l(R) C_m^{(l)}(\Omega) = (-1)^m \sum_k \hat{A}_{lk} \Phi_l(R) \begin{pmatrix} k & 1 & l \\ m-\mu & \mu & -m \end{pmatrix} C_{m-\mu}^{(k)}(\Omega) \quad (10)$$

and

$$\begin{aligned} & \frac{\partial^2}{\partial R_\mu \partial R_{\mu'}} \Phi_l(R) C_m^{(l)}(\Omega) \\ &= (-1)^\mu \sum_{k'} \sum_k \hat{A}_{kk'} \hat{A}_{lk} \Phi_l(R) \begin{pmatrix} k' & 1 & k \\ m-\mu-\mu' & \mu' & -m+\mu \end{pmatrix} \\ & \quad \times \begin{pmatrix} k & 1 & l \\ m-\mu & \mu & -m \end{pmatrix} C_{m-\mu-\mu'}^{(k')}(\Omega) \end{aligned} \quad (11)$$

where the operator \hat{A}_{lk} is defined as

$$\begin{aligned} \hat{A}_{lk} &= (-1)^l \left[\delta_{k,l-1} \left(\frac{l(2l-1)}{2l+1} \right)^{1/2} \left(\frac{d}{dR} + \frac{l+1}{R} \right) \right. \\ & \quad \left. - \delta_{k,l+1} \left(\frac{(l+1)(2l+3)}{2l+1} \right)^{1/2} \left(\frac{d}{dR} - \frac{l}{R} \right) \right]. \end{aligned} \quad (12)$$

The derivatives with respect to spherical tensor components $R_{p\mu}$ and $R_{p'\mu}$ have to be transformed into cartesian derivatives. By the use of (8) together with the property that the pair potential $V_{pp'}$ is a real function, it is easily shown that the cartesian translation-rotation force constants $F_{pp'}^{\tau\rho}$ ($\tau = x, y, z$; $\rho = \vartheta, \varphi$) are related to the spherical tensor components $F_{pp'}^{\mu\rho}$ ($\mu = -1, 0, 1$) via

$$F_{pp'}^{x\rho} = -\sqrt{2} \operatorname{Re} \left[F_{pp'}^{1\rho} \right] \quad F_{pp'}^{y\rho} = \sqrt{2} \operatorname{Im} \left[F_{pp'}^{1\rho} \right] \quad F_{pp'}^{z\rho} = F_{pp'}^{0\rho}. \quad (13)$$

The cartesian translation second derivatives $F_{pp'}^{\tau\tau'}$ can be obtained from the spherical tensor components $F_{pp'}^{\mu\mu'}$ using the relations

$$\begin{aligned} F_{pp'}^{xx} &= -F_{pp'}^{-11} + \text{Re} [F_{pp'}^{11}] & F_{pp'}^{xy} &= F_{pp'}^{yx} = -\text{Im} [F_{pp'}^{11}] \\ F_{pp'}^{yy} &= -F_{pp'}^{-11} - \text{Re} [F_{pp'}^{11}] & F_{pp'}^{xz} &= F_{pp'}^{zx} = -\sqrt{2} \text{Re} [F_{pp'}^{10}] \\ F_{pp'}^{zz} &= F_{pp'}^{00} & F_{pp'}^{yz} &= F_{pp'}^{zy} = \sqrt{2} \text{Im} [F_{pp'}^{10}]. \end{aligned} \quad (14)$$

Herewith, we have given some basic analytical formulas that can be combined in order to evaluate the force constants corresponding to a spherically expanded intermolecular pair potential. These formulas will also be useful in applications of anisotropic atom-atom potentials [8–10]. The force constants have been implemented in a harmonic lattice dynamics program in which they are used to construct the wave-vector-dependent dynamical matrix [21]. Diagonalization of this matrix yields the desired lattice vibration frequencies.

3. Results and discussion

We have performed harmonic lattice dynamics calculations on α - and γ -nitrogen using a spherical expansion of the intermolecular potential as described in section 2. The self-term has been evaluated either as a lattice sum of second derivatives, see (3), or with translational and rotational invariance conditions [21–23], which yields identical results. Further test calculations have been performed with the exp-6-1 atom-atom model B of [15], which we have transformed into a spherical expansion using analytical formulas for the long-range dispersion [25] and electrostatic interactions [4] and a fitting procedure for the short-range exponential terms. The resulting lattice vibration frequencies differ at most by 0.2 cm^{-1} from standard harmonic calculations, in which the force constants are evaluated via direct analytical derivatives of atom-atom potentials. These minor differences are probably due to fitting inaccuracies.

In table 1 experimental and calculated phonon frequencies are presented for α -N₂. It is observed that in particular the harmonic libron frequencies, obtained with the atom-atom model fitted to the *ab initio* potential, are too high compared with experiment (RMS deviation 12.7 cm^{-1}). A similar deviation of the libron frequencies was obtained with the best empirical atom-atom potential from [1], whereas the translational phonon frequencies agreed well with experiment (see table 1; note that the parameters in this empirical atom-atom potential have been fitted [1] to the lattice frequencies). As mentioned in section 1, this discrepancy was believed to be due mainly to the failure of the harmonic model, because of large-amplitude angular motions. Now we find, however, that the harmonic calculations which use the direct spherical expansion of the *ab initio* potential of [15], i.e. without intervention of an atom-atom model, are in excellent agreement with experiment, even for the angular modes with an RMS deviation of 5.4 cm^{-1} . Apparently, the direct spherical expansion provides a substantially better description of the potential anisotropy than the atom-atom potential. This plays an important role in the rotational dynamics. In addition, the translational lattice vibrations are also better described (1.3 cm^{-1} RMS deviation). Optimization of the crystal structure, within the cubic *Pa3* symmetry, increases the deviations slightly.

Table 1. Lattice vibration frequencies in α -N₂ (in cm⁻¹) from experiment, semi-empirical SE and *ab initio* calculations.

		Expt ([26])	SE ([1])	<i>Ab initio</i>					
				Atom-atom		Spherical expansion			
				Harmonic		Harmonic	TDH [18]		
Lattice constant	a (Å)	5.644	5.644	5.644	5.611†	5.644	5.588†	5.644	5.699†
$\Gamma(0,0,0)$									
Librations	E _g	32.3	37.5	40.7	42.4	27.6	29.7	32.8	31.0
	T _g	36.3	47.7	50.9	52.8	41.6	44.3	43.4	41.0
	T _g	59.7	75.2	75.2	77.6	67.9	71.6	71.5	68.0
Translational vibrations	A _u	46.8	45.9	50.2	52.7	44.2	47.8	50.6	47.2
	T _u	48.4	47.7	49.8	52.6	46.8	51.1	52.7	48.8
	E _u	54.0	54.0	55.8	58.9	54.8	59.8	60.2	55.6
	T _u	69.4	69.5	74.3	78.8	70.4	77.5	79.4	73.1
$M(\pi/a, \pi/a, 0)$									
Mixed	M ₁₂	27.8	29.6	33.4	34.9	24.2	25.0	28.8	27.6
	M ₁₂	37.9	40.6	44.3	46.3	36.2	39.0	41.5	39.1
	M ₁₂	46.8	51.8	56.6	59.0	49.8	53.2	53.3	50.2
	M ₁₂	54.9	59.0	61.3	64.4	58.5	63.8	63.7	59.1
	M ₁₂	62.5	66.4	68.6	72.2	65.6	71.6	72.0	66.5
$R(\pi/a, \pi/a, \pi/a)$									
Translational vibrations	R ₁ ⁻	33.9	34.4	35.3	37.1	33.5	36.4	37.0	34.4
	R ₂₃ ⁻	34.7	35.7	37.3	39.2	34.6	37.4	38.4	35.8
	R ₂₃ ⁻	68.6	68.3	73.0	77.6	69.4	76.6	78.4	72.3
Librations	R ₁ ⁺	43.6	50.7	55.9	58.0	48.6	51.7	50.7	47.9
	R ₂₃ ⁺	47.2	57.8	58.8	60.9	49.5	52.3	53.6	50.8
RMS deviation of librational frequencies			10.6	12.7	14.9	5.4	7.6	7.5	5.0
RMS deviation of translational frequencies			0.6	3.1	6.3	1.3	5.6	6.5	2.1
RMS deviation of all lattice frequencies			6.1	8.1	10.4	3.1	6.5	6.7	3.4

† Obtained via minimization of the lattice energy.

It is interesting to compare the harmonic lattice vibration frequencies with TDH results [18], also included in table 1, which are obtained with the same spherical expansion of [15]. This comparison yields directly the anharmonic shifts in the lattice frequencies. The TDH libron frequencies are higher, by 1.8 up to 5.2 cm⁻¹, than the corresponding harmonic values, which increases the discrepancy with experiment from 5.4 to 7.5 cm⁻¹ if the experimental lattice constant is used ($a = 5.644$ Å). Further, the translational RMS deviation is increased from 1.3 to 6.5 cm⁻¹, which appears to be mainly due to third- and fourth-order anharmonic terms in the potential expansion with respect to molecular displacements [18]. The upward anharmonic shifts of the lattice frequencies are in good agreement with the shifts obtained from Green function calculations [27–29]. Optimization of the crystal structure lowers the TDH frequencies. The resulting overall deviation is 3.4 cm⁻¹, which is almost equal to the harmonic deviation of 3.5 cm⁻¹ (at the experimental structure).

In addition, we have performed TDH calculations with the atom-atom potential model B of [15], via the spherical expansion used in the test calculations described

Table 2. Lattice vibration frequencies in γ -N₂ (in cm⁻¹).

		Expt ([26])	Semi- empirical ([1])	<i>Ab initio</i>					
				Atom-atom		Spherical expansion			
				Harmonic		Harmonic		TDH [18]	
Lattice constant	<i>a</i> (Å)	3.957	3.940	3.957	4.181†	3.957	4.039†	3.957	3.961†
Lattice constant	<i>c</i> (Å)	5.109	5.086	5.109	5.126†	5.109	5.246†	5.109	5.104†
Γ(0,0,0)									
Librations	E _g	55.0	50.5	56.0	48.6	65.7	54.4	67.5	67.6
	B _{1g}	98.1	74.8	101.8	70.6	102.1	89.1	104.2	103.3
	A _{2g}	—	105.1	122.5	92.4	118.3	103.2	125.1	124.4
Translational vibrations	E _u	65.0	58.3	68.6	55.7	58.1	47.9	65.0	65.2
	B _{1u}	—	103.1	112.2	83.2	106.0	86.0	115.8	114.9
RMS deviation			14.2	3.0	17.2	7.7	11.2	8.0	7.9

† Obtained via minimization of the lattice energy.

above. This shows a similar deviation from experiment as the harmonic atom-atom results; in particular the TDH libron frequencies in α -nitrogen calculated with the atom-atom potential came out about 30% too high. So, we conclude that the substantial differences between harmonic and TDH results found earlier [17, 18] are mostly due to the different modellings of the *ab initio* potential, especially of its anisotropy. Lattice dynamics calculations on the γ -phase, where the librational motions are more strongly localized, yield a similar conclusion (see table 2). Apparently, the specific strength of TDH lies not so much in the low-temperature dynamics of ordered molecular crystals, but rather in the description of disordered phases (β -nitrogen [30], for example), quantum crystals (solid hydrogen [31]) and the combination of lattice dynamics with spin waves (in solid oxygen [2]).

Acknowledgments

This investigation was supported partly by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

References

- [1] Raich J C and Gillis N C 1977 *J. Chem. Phys.* **66** 846
- [2] Briels W J, Jansen A P J and van der Avoird A 1986 *Adv. Quantum Chem.* **18** 131
- [3] Scott T A 1976 *Phys. Rep.* **27** 89
- [4] Rose M E 1958 *J. Math. Phys.* **37** 215
- [5] Pertsin A J and Kitaigorodski A I 1987 *The Atom-Atom Potential Method for Organic Molecular Solids* (Berlin: Springer)
- [6] Filippini G, Grammacioli C M, Simonetta M and Suffritti G B 1978 *Mol. Phys.* **35** 1659
- [7] Burgos E, Murthy C S and Righini R 1982 *Mol. Phys.* **47** 1391
- [8] Price S L and Stone A J 1982 *Mol. Phys.* **47** 1457
- [9] Rodger P M, Stone A J and Tildesley D J 1987 *J. Chem. Soc. Trans. Faraday Trans. II* **83** 1689

- [10] Stone A J and Price S L 1988 *J. Phys. Chem.* **92** 3325
- [11] Luty T, van der Avoird A and Berns R M 1980 *J. Chem. Phys.* **73** 5305
- [12] van der Avoird A, Wormer P E S, Mulder F and Berns R M 1980 *Top. Curr. Chem.* **93** 1
- [13] Nyeland C, Poulsen L L, and Billing G D 1984 *J. Phys. Chem.* **88** 1216
- [14] Corbin N, Meath W J, and Allnatt A R 1984 *Mol. Phys.* **53** 225
- [15] Berns R M and van der Avoird A 1980 *J. Chem. Phys.* **72** 6107
- [16] Werthamer N R 1976 *Rare Gas Solids* ed M L Klein and J Venables (London: Academic)
- [17] Jansen A P J, Briels W J and van der Avoird A 1984 *J. Chem. Phys.* **81** 3648
- [18] Briels W J, Jansen A P J and van der Avoird A 1984 *J. Chem. Phys.* **81** 4118
- [19] Edmonds A R 1957 *Angular Momentum in Quantum Mechanics* (Princeton, NJ: Princeton University Press)
- [20] van der Avoird A, Wormer P E S and Jansen A P J 1986 *J. Chem. Phys.* **84** 1629
- [21] Califano S, Schettino V and Neto N 1981 *Lattice Dynamics of Molecular Crystals* (Berlin: Springer)
- [22] Neto N, Taddei G, Califano S and Walmsley S H 1976 *Mol. Phys.* **31** 457
- [23] Neto N and Kirin D 1979 *Chem. Phys.* **44** 245
- [24] Varshalovich D A, Moskalev A N and Chersonskij V K 1975 *Quantum Theory of Angular Momentum* (Leningrad: Nauka)
- [25] Yasuda H and Yamamoto T 1971 *Prog. Theor. Phys.* **45** 1458
- [26] Kjems J K and Dolling G 1975 *Phys. Rev. B* **11** 1639
- [27] Kobashi K 1978 *Mol. Phys.* **36** 225
- [28] Signorini G F, Fracassi P F, Righini R and Della Valle R G 1985 *Chem. Phys.* **100** 315
- [29] Gonçalves S and Bonadeo H 1986 *J. Chem. Phys.* **84** 4106
- [30] van der Avoird A, Briels W J and Jansen A P J 1984 *J. Chem. Phys.* **81** 3658
- [31] Janssen W B J M and van der Avoird A 1990 *Phys. Rev. B* **42** 838