Journal of Quantitative Spectroscopy & Radiative Transfer 209 (2018) 232–242

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Multi-property isotropic intermolecular potentials and predicted spectral lineshapes of collision-induced absorption (CIA), collision-induced light scattering (CILS) and collision-induced hyper-Rayleigh scattering (CIHR) for H_2−Ne, −Kr and −Xe

M.S.A. El-Kader[a,b,*], J.-L. Godet[c], M. Gustafsson[d], G. Maroulis[e]

[a] Department of Engineering Mathematics and Physics, Faculty of Engineering, Cairo University, Giza 12211, Egypt
[b] Department of Physics, Faculty of Sciences and Humanity Studies, Huraimla, Shaqra University, Shaqra, Saudi Arabia
[c] Laboratoire de photonique d'Angers, Université d'Angers, 2 boulevard Lavoisier, Angers 49045, France
[d] Department of Engineering Sciences and Mathematics, Luleå University of Technology, Luleå SE-97187, Sweden
[e] Department of Chemistry, University of Patras, Patras GR-26500, Greece

ARTICLE INFO

Article history:
Received 25 December 2017
Revised 29 January 2018
Accepted 30 January 2018

Keywords:
Induced dipole moment
Intermolecular potential
CIA
CILS
CIHR

ABSTRACT

Quantum mechanical lineshapes of collision-induced absorption (CIA), collision-induced light scattering (CILS) and collision-induced hyper-Rayleigh scattering (CIHR) at room temperature (295 K) are computed for gaseous mixtures of molecular hydrogen with neon, krypton and xenon. The induced spectra are detected using theoretical values for induced dipole moment, pair-polarizability trace and anisotropy, hyperpolarizability and updated intermolecular potentials. Good agreement is observed for all spectra when the literature and the present potentials which are constructed from the transport and thermo-physical properties are used.

1. Introduction

Collision-induced absorption spectra correspond to transitions forbidden in an isolated molecular species which appear when it is found in the form of compressed gas, liquid, or solid. An induced infrared absorption spectrum was first identified by Bosomworth and Gush [1] in liquid and compressed hydrogen. It was recognized that the molecular vibrations and rotations become infrared active because of electric dipole moments induced in colliding pairs of molecules by intermolecular forces. The dipole moment depends in magnitude on the intermolecular distance and in direction on the orientations of the colliding moieties.

Collisional pairs of molecules in dense phase show an absorption band in the far infrared region of the spectrum [2–5]. This absorption is due to the induced dipole moment $\mu(r)$ arising from the distortion of the electronic clouds during the collision of two molecules. As the induced dipole moment depends on the distance between the colliding pair, the translational state of the system can change due to the interaction of the induced dipole with the electromagnetic field, giving rise to a rototranslational absorption band. Measurements of collision-induced absorption (CIA) spectra give therefore information on intermolecular interactions. Specifically, spectral lineshapes and intensities reflect certain details of the induced dipole as function of the interatomic separation and the collision dynamics (i.e. the intermolecular potential).

The isotropic and anisotropic collision-induced light scattered by a fluid or dense gas due to collisional interactions have power spectra which are shaped by two functions of the intermolecular separation r, the interaction potential V(r), and, respectively, the trace $\alpha(r)$ and the anisotropy $\beta(r)$ of the induced polarizability [6–11]. In a gas at moderate pressures the isotropic and anisotropic spectra are determined by binary interactions only and are proportional to the Fourier transform of the pair correlation function.

In the case of gases consisting of optically isotropic atoms, pure collision-induced anisotropic spectra are observed in the vicinity of the Rayleigh line where no monoatomic scattering is allowed [8]. Information on the atomic interactions may be obtained from these spectra. For the lower-frequency part of these spectra, the

---

[*] Corresponding author at: Department of Engineering Mathematics and Physics, Faculty of Engineering, Cairo University, Giza 12211, Egypt.

E-mail address: mohamedsay68@hotmail.com (M.S.A. El-Kader).

https://doi.org/10.1016/j.jqsrt.2018.01.035

dipole-induced-dipole (DID) interaction accounts for most of the observed scattering intensities, whereas, at high frequency range (the well region of the intermolecular potential), electron exchange contributions have to be taken into account and can thus be measured for all rare gas diatoms against the dominating classical DID background [8,12]. Recently, the spectral properties of isotropic and anisotropic interaction-induced light scattering were calculated for both the gaseous monoatomic, linear and polyatomic molecules, on the basis of classical, empirical or ab initio models of the induced trace and anisotropy, and of the interaction potential [13–22].

On another level, collision-induced rototranslational hyper-Rayleigh spectra of gaseous H_2–inert gas mixtures at room temperature are computed and discussed in the binary regime using the *ab initio* computed collision-induced first dipole hyperpolarizability tensor [23–26]. Last, we mention the magisterial treatment of the interaction polarizability of hydrogen molecule with inert gas mixtures [27,28] and the calculation of the isotropic and anisotropic collision-induced rototranslational Raman light scattering spectra, reported by Glaz et al. [10,11].

No adequate potential with the parameters fitted well with the different thermophysical and transport properties at different temperatures is available to study the gas phase of systems under consideration. We calculate the intermolecular potential for the H_2–Ne, –Kr and –Xe interaction using mostly the methods outlined in previous work [29,30]. Only a few essential details are given here. To reiterate, our basic strategy is to include the data on second pressure virial coefficients, viscosity, diffusion, thermal conductivity and thermal diffusion factor data at wide range of temperatures to fit the simple functional form of the intermolecular potential for H_2–inert gas interactions.

The thermo-physical and transport properties used in the fitting are complementary ones for that purpose. For these pairs of gas molecules, the measured Pressure virial coefficients reflect the size of r_m and the volume of the attractive well [31], while the viscosity, thermal conductivity and diffusion data are most sensitive to the wall of the potential from r_m inward to a point where the potential is repulsive [32].

Spectral profiles of both scattering and absorption are calculated numerically with the help of a quantal computer program, and compared to the recent calculated spectra. The comparison of calculated and measured spectra provides valuable insights on the quality of existing models of both the interaction-induced trace and anisotropy polarizability for scattering and the dipole moments and the intermolecular potential for absorption. Calculations of the different thermophysical and transport properties at different temperatures using different intermolecular potential models are presented in Sections 2–4. The theoretical method for the calculation of the spectral lineshapes intensities of collision-induced absorption, isotropic, anisotropic and hyper-Rayleigh induced light scattering with the ab initio forms of the dipole moment, diatom trace and anisotropy polarizability and hyper-polarizability is briefly given in Section 5, together with the computational implementation. The concluding remarks are given in Section 6.

2. Thermo-physical and transport properties

In order to calculate the line profiles of absorption and scattering and their associated moments, the intermolecular potential is needed. Results with different potentials can be compared with experiment to assess the quality of the potential.

The intermolecular potential we provide here is obtained through the analysis of the second pressure virial coefficients [33–37], viscosity, thermal conductivity, diffusion coefficients and thermal diffusion factors [38–44].

For the analysis of all these experimental data we consider the Barker, Fisher and Watts (BFW) potential [45],

$$V(r) = \varepsilon\left(\sum_{i=0}^{5} \mathrm{B_i}(\mathrm{r}/\mathrm{r_m}-1)^i \exp(\xi(1-\mathrm{r}/\mathrm{r_m})) - \sum_{i=0}^{2}\frac{\mathrm{C_{2i+6}}}{\left((\mathrm{r}/\mathrm{r_m})^{2i+6}+\mathrm{del}\right)}\right) \tag{1}$$

where ε is the potential depth, r_m is the distance at the minimum potential and the rest are fitting parameters.

Even at the present (BFW) level, there are really thirteen parameters (ε, r_m, B_0, B_1, B_2, B_3, B_4, B_5, ξ, del, C_6, C_8, and C_{10}) which are far too many to determine from the present data. Accordingly we proceeded as follows: the coefficients B_0 and B_1 are determined from the conditions of continuity and the long-range dispersion coefficients C_6, C_8 and C_{10} were taken from theoretical calculations of Tang and Toennies [46,47], leaving eight parameters (ε, r_m, B_2, B_3, B_4, B_5, ξ, and del) that were varied to fit the second pressure virial coefficients. This fitting is further supported by calculating the viscosity, diffusion coefficient, thermal conductivity and thermal diffusion factor. Calculations were speeded by determining rough values of these parameters and then final convergence was obtained by iteration with the full isotropic and anisotropic potentials. This decision leads to potential parameters of Table 1 as our best estimate of H_2-inert gas mixtures intermolecular potentials.

In addition to the present potential, some older empirical Lennard–Jones, Buckingham–Corner (BC), HFD, TT_3 and Morse isotropic potentials [35,48–57], as well as the MSV and ab initio potentials [38,58] were considered.

3. Analysis of second pressure virial coefficients

An effective means for checking the validity of the different potential parameters is to use second pressure virial coefficient data [33–37] at different temperatures. The interaction second pressure virial coefficient B_{12} at temperature T was calculated classically with the first three quantum corrections from [59,60]:

$$\mathrm{B_{12}(T) = B_{cl}(T) + \lambda B_{qm,1}(T) + \lambda^2 B_{qm,2}(T) + \lambda^3 B_{qm,3}(T)} \tag{2}$$

where

$$\mathrm{B_{cl}(T)} = 2\pi \mathrm{N_o}\int_0^\infty [1-\exp(-\mathrm{V(r)/kT})]\mathrm{r^2dr} \tag{3}$$

and the first three quantum corrections $B_{qm,\,1}(T)$, $B_{qm,2}(T)$ and $B_{qm,\,3}(T)$ are given in Ref. [61], with $\lambda = \hbar^2/(12mkT)$, $\hbar = h/2\pi$, m and N_A are the mass number and Avogadro's number. The calculated B_{12} was compared with the experimental results [33–37] using the present BFW and different intermolecular potentials [35,38,48–57]. As it may be clearly seen in Figs. 1–3 and Table 1, the isotropic BFW potentials give the best agreement with the experimental values over a high range of temperatures.

4. Analysis of traditional transport properties

An additional check on the proposed potential consists of the calculation of the transport properties i.e. viscosity $\eta(T)$, diffusion coefficient D(T), isotopic thermal factor $\alpha_T(T)$ and thermal conductivity $\lambda(T)$ at different temperatures of these systems. These are obtained via the formulae of Monchick et al. [61] and their comparison to the accurate experimental and theoretical results [38–44] which are clear by calculating the associated values of δ_a as shown in Table 1. The agreements for all systems under consideration are excellent in the whole temperature range.

5. Theory of rototranslational collision-induced spectra

In this section we described the quantum mechanical calculations for collision-induced absorption (CIA), collision-induced