Calculated isotropic Raman spectra from interacting H$_2$–rare-gas pairs

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Abstract. We report on a theoretical study of the H$_2$–He and H$_2$–Ar pair trace-polarizability and the corresponding isotropic Raman spectra. The conventional quantum mechanical approach for calculations of interaction-induced spectra, which is based on an isotropic interaction potential, is employed. This is compared with a close-coupling approach, which allows for inclusion of the full, anisotropic potential. It is established that the anisotropy of the potential plays a minor role for these spectra. The computed isotropic collision-induced Raman intensity, which is due to dissimilar pairs in H$_2$–He and H$_2$–Ar gas mixtures, is comparable to the intensities due to similar pairs (H$_2$–H$_2$, He–He, and Ar–Ar), which have been studied previously.

1. Introduction

Light propagating through a molecular medium can be attenuated by absorption, reflection and scattering. In light scattering the polarizability tensor of the molecule determines the response to the incident radiation and thereby the intensity and polarization of scattered radiation. Mathematically the polarizability tensor can be decomposed into its isotropic (trace) part and the traceless (anisotropy) part. Following this partition the light scattering intensity is a sum of a polarized (isotropic) and a depolarized part stemming from the trace and the anisotropy of the polarizability, respectively [1].

The polarizability of an interacting pair is different from the sum of the unperturbed monomers' polarizabilities. This results in so-called collision-induced, or interaction-induced, light scattering which is density-dependent and relatively weak at atmospheric pressures. Modern techniques for measurement of light scattering are, however, so refined that the signals due to interacting pairs can be detected [2]. Theoretical and experimental studies of such spectra give insight into the fundamental interactions and properties of molecular systems.

In this work we report on the interaction-induced trace polarizability and the isotropic light scattering spectra for H$_2$–He and H$_2$–Ar complexes. A more complete presentation, which includes three more H$_2$–rare-gas systems, is available in Ref. [3]. In that work we also compared a classical approach with the quantum mechanical methods used here for the calculations of spectra. We will not elaborate on this further, but note that for the systems we studied
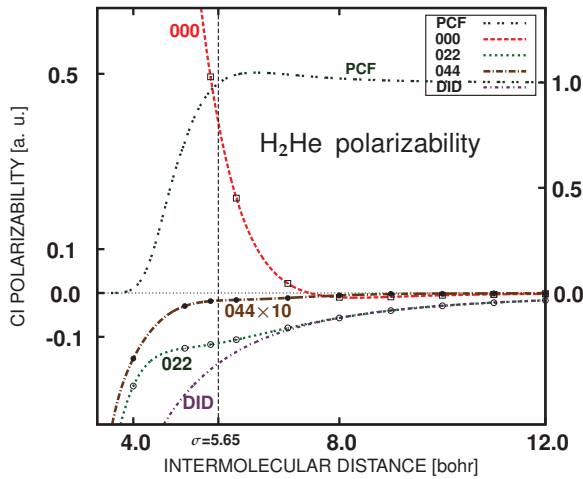
Figure 1. H$_2$–He trace polarizability components $\Delta\alpha^{(0)}_{\lambda\lambda}(R)$. Reprinted with permission from [3]. Copyright (2014), American Institute of Physics.
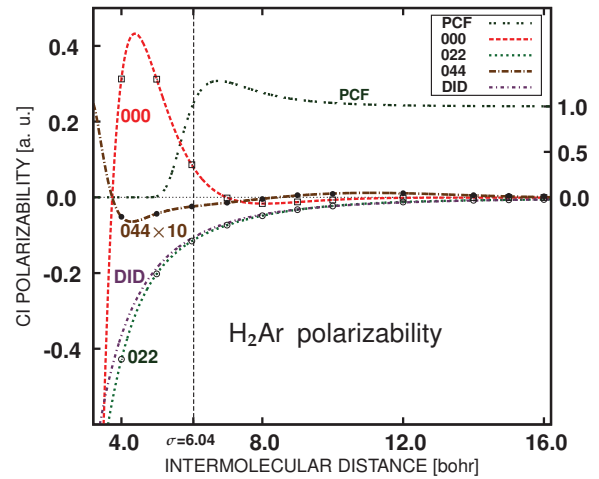

Figure 2. H$_2$–Ar trace polarizability components $\Delta\alpha^{(0)}_{\lambda\lambda}(R)$. Reprinted with permission from [3]. Copyright (2014), American Institute of Physics.

calculations based on classical trajectories may be used if the desired level of accuracy is less than about 6 percent.

2. Calculations

The interaction-induced polarizability may be computed with *ab initio* methods and expanded according to

$$\Delta\alpha^{(K)}_{\mu}(\hat{\mathbf{r}}, \mathbf{R}) = \frac{4\pi}{\sqrt{2K+1}} \sum_{\lambda L} \Delta\alpha^{(K)}_{\lambda L}(R) \, Y^{K\mu}_{\lambda L}(\hat{\mathbf{r}}, \hat{\mathbf{R}}) \tag{1}$$

where the angular functions are defined as

$$Y^{K\mu}_{\lambda L}(\hat{\mathbf{r}}, \hat{\mathbf{R}}) = \sum_{m_\lambda m_L} C(\lambda, L, K; m_\lambda, m_L, \mu) \, Y_{\lambda m_\lambda}(\hat{\mathbf{r}}) \, Y_{L m_L}(\hat{\mathbf{R}}) \tag{2}$$

with C and Y being Clebsch-Gordan coefficients and spherical harmonics, respectively. $\mathbf{R}$ is the vector pointing from the center of mass of the H$_2$-molecule to the rare-gas atom and $\hat{\mathbf{r}}$ is the unit vector specifying the orientation of the H$_2$-molecule. The r-dependence does not appear in Eq. (1) since it is averaged over. In other words, we do not consider vibrational excitations of H$_2$. The polarized (isotropic) light scattering [1] is due to the trace components $\Delta\alpha^{(0)}_{\lambda\lambda}(R)$ which are shown with $\lambda = 0, 2, 4$ for H$_2$–He and H$_2$–Ar in Figs. 1 and 2, respectively. The dipole-induced-dipole (DID) approximation for the 022 component is also displayed for both systems, showing that it works better for the Ar-system than for the He-system. In addition the pair correlation function (PCF) and collision diameter (σ) are presented.

In our calculations of light scattering intensity we have used the interaction potentials from [4] and [5] for H$_2$–He and H$_2$–Ar, respectively. First, we assume that those interaction potentials are isotropic, i.e. $V(\hat{\mathbf{r}}, \mathbf{R}) = V(R)$. This is straightforward to do if they have been expanded in angular functions in the standard way [6]. Then the spectra can be computed by evaluation and proper thermal weighting of the squared matrix elements [7]

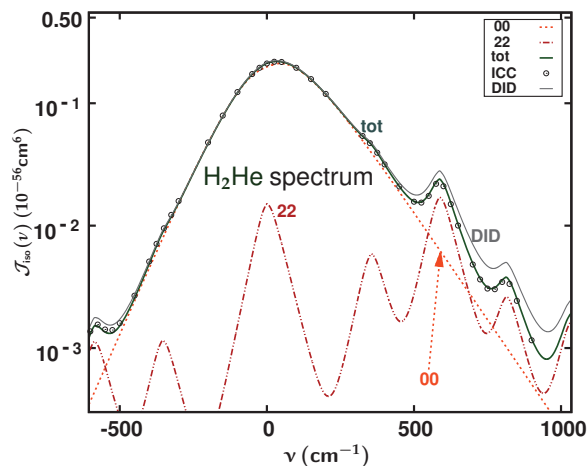$$\left| \int \psi_i(R) \, \Delta\alpha^{(0)}_{\lambda\lambda}(R) \, \psi_f(R) \, dR \right|^2$$

Figure 3. H$_2$–He polarized light scattering spectrum. Reprinted with permission from [3]. Copyright (2014), American Institute of Physics.
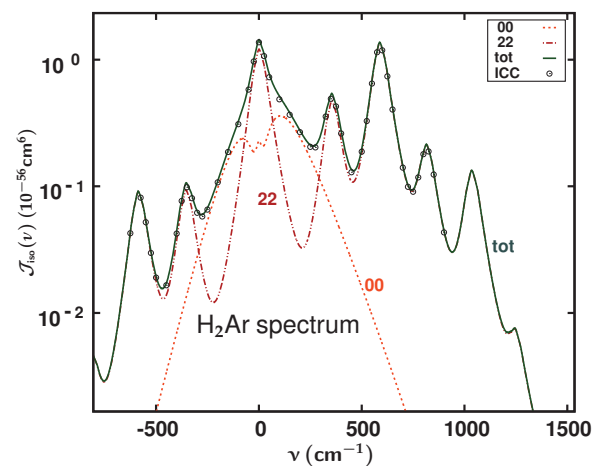

Figure 4. H$_2$–Ar polarized light scattering spectrum. Reprinted with permission from [3]. Copyright (2014), American Institute of Physics.

where ψ_i and ψ_f are the initial and final continuum wave functions, respectively. In this case it is thus sufficient to solve a one-dimensional Schrödinger equation in the R-coordinate to obtain the continuum functions. In Figs. 3 and 4 the calculated polarized light scattering spectra are shown. The 000 component of the trace polarizability accounts for the vast majority of the intensity in the H$_2$–He case, while for H$_2$–Ar it is the 022 component that dominates. For H$_2$–He the result based on the DID 022 component is also displayed, which causes an overestimation of the intensity for frequency shifts larger than about 500 cm^{-1}.

Second, we account for the full (anisotropic) potential, $V(\hat{\mathbf{r}}, \mathbf{R})$, by using the close-coupling scheme to obtain S-matrix elements corresponding to light scattering [8, 9]. The electromagnetic field and its coupling with the molecular system (through the interaction-induced polarizability) are included explicitly in the Hamiltonian. This results in a coupled system of Schrödinger equations in the R-coordinate. The anisotropy of the potential may be excluded in this scheme and we have labeled such calculations ICC (isotropic close-coupling) and included the resulting spectra in Figs. 3 and 4. Those calculations are clearly consistent with the conventional quantum calculations, as they should be, and we can trust that both methods are correctly implemented. In Fig. 5 comparisons of spectra obtained with and without the anisotropy of the interaction potential are displayed for both systems. It turns out that the anisotropy only affects the spectra by a few percent for both the H$_2$–He and H$_2$–Ar systems, with a slightly larger effect on the latter.

3. Conclusions

The polarized Raman intensities for the H$_2$–rare-gas systems studied in this work are on the same order of magnitude as the intensities due to the corresponding similar pairs H$_2$–H$_2$, He–He, and Ar–Ar, which have been studied before, e.g. in Refs. [7, 10, 11]. It should thus be possible to extract the H$_2$–rare-gas isotropic spectra from light scattering experiments with hydrogen gas mixed with helium or argon. The conventional quantum calculations, which are based on the distorted wave approximation and an isotropic interaction potential, agree with close-coupling calculations when the anisotropy of the potential is excluded in the latter. Full close-coupling calculations show that the anisotropy of the interaction potential only plays a role on the few percent level for the isotropic Raman spectra of the H$_2$–He and H$_2$–Ar systems.
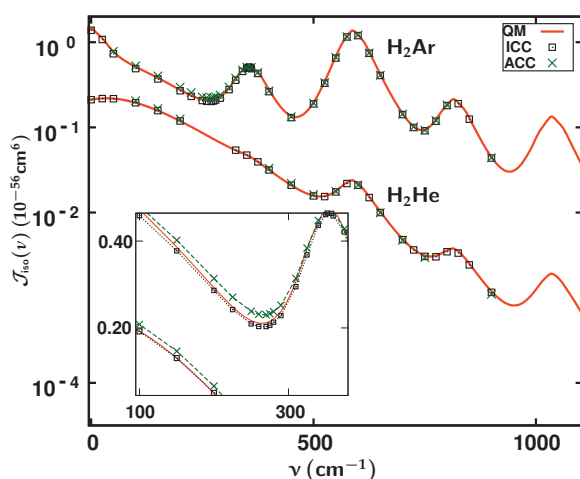
Figure 5. Isotropic light scattering intensity for H_2–He and H_2–Ar, displaying the influence on the spectra from the anisotropy of the potential. QM indicates conventional quantum calculations. ICC and ACC indicate close-coupling calculations with isotropic and anisotropic interaction potential, respectively. Reprinted with permission from [3]. Copyright (2014), American Institute of Physics.

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