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Collision-Induced Absorption by Supermolecular Complexes from a New Potential Energy and Induced Dipole Surface, Suited for Calculations up to Thousands of Kelvin

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Abstract. Absorption by pairs of H₂ molecules is an important opacity source in the atmospheres of the outer planets, and thus of special astronomical interest. The emission spectra of cool white dwarf stars differ significantly from the expected blackbody spectra, amongst other reasons due to absorption by H₂-H₂, H₂-He, and H₂-H collisional complexes in the stellar atmospheres. To model the radiative processes in these atmospheres, which have temperatures of several thousand kelvin, one needs accurate knowledge of the induced dipole (ID) and potential energy surfaces (PES) of such collisional complexes. These come from quantum-chemical calculations with the H₂ bonds stretched or compressed far from equilibrium. Laboratory measurements of collision-induced (CI) absorption exist only at much lower temperature. For H₂ pairs at room temperature, the calculated spectra of the rototranslational band, the fundamental band, and the first overtone match the experimental data very well. In addition, with the newly obtained IDS it became possible to reproduce the measurements in the far blue wing of the rototranslational spectrum of H₂ at 77.5 K, as well as at 300 K. Similarly good agreement between theory and measurement is seen in the fundamental band of molecular deuterium at room temperature. Furthermore, we also show the calculated absorption spectra of H₂-He at 600 K and of H₂-H₂ at 2,000 K, for which there are no experimental data for comparison.

Keywords: Collision-induced absorption, induced dipole and potential energy surfaces for H₂-H₂ and H₂-He, cool white dwarf stars

PACS: 34.10.+x, 34.50.-s, 34.50.Ez, 36.20.Ng, 95.30.Ft, 95.30.Ky, 95.35.+d, 97.20.Vs

INTRODUCTION

Dense gases of infrared inactive molecules such as H₂ absorb infrared radiation, due to collision-induced (CI) transient electric dipole moments, which are responsible for most of the observed absorption continua [1, 2]. Absorption ranges from the microwave and far infrared regions of the electromagnetic spectrum to the near infrared and visible. Early on, planetary researchers understood the significance of modelling CI absorp-

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tion for the outer planets [3]. More recently, it was found that the emission spectra of cool white dwarf stars differ substantially from the expected blackbody spectra, amongst other reasons due to CI absorption in the dense hydrogen and helium dominated atmospheres [4–9]; see also the contribution by L. Frommhold *et al.* in this volume. For an accurate theoretical description of the atmospheres of cool stars CI opacities can certainly not be ignored, but proper modeling of the radiative profiles has been hampered heretofore by highly incomplete or nonexistent theoretical and experimental data on such opacities at elevated temperatures.

In the past, the CI dipoles and potential energy surfaces (PES) of $\text{H}_2\text{-H}_2$, $\text{H}_2\text{-He}$ and other complexes have been calculated successfully using quantum-chemical methods [10–13]. Molecular scattering calculations taking into account interactions with photons based on such data accurately reproduced existing laboratory measurements at and below room temperature [1]. At higher temperatures, no suitable laboratory measurements of CI opacities exist. However, astrophysicists have an urgent need to correct their observational data of "cool" white dwarf star emission spectra for CI absorption in the star atmospheres. Hence, our group has started to compute the binary CI absorption of supermolecular complexes such as $\text{H}_2\text{-H}_2$, $\text{H}_2\text{-He}$, and $\text{H}_2\text{-H}$ at frequencies from 0 to 20,000 cm^{-1} in steps of 20 cm^{-1} and temperatures from 300 to 7,000 K in steps of 25 K from first principles, for use by astrophysical specialists. Extensive tables of opacity data are being created and will be made available to interested parties upon request.

At the frequencies and temperatures of interest, the strong rotovibrational excitations of the involved molecules can certainly not be ignored [12]. Therefore, it is necessary to extend the earlier quantum-chemical calculations of the induced dipoles (ID) and PES of $\text{H}_2\text{-H}_2$ and $\text{H}_2\text{-He}$ complexes to cover highly rotovibrationally excited molecules, as encountered at the temperatures of up to 7,000 K and photon energies up to 2.5 eV. The PES and IDS were determined completely *de novo* and over an enlarged set of conditions, and the existing computer codes had to be modified. Therefore, it is in order to perform several checks before proceeding to the temperatures and frequencies of interest.

CI ABSORPTION SPECTRA

At the above mentioned temperatures and frequencies, the CI absorption spectra depend on transition dipole matrix elements with vibrational quantum numbers up to $v \approx 7$. Rotational quantum numbers j range up to 20 for H_2 molecules under these conditions.

To compute CI absorption spectra over the whole frequency range considered, one has to compute the contributions from several hundred thousand optical transitions from an initial state $v_1 j_1 v_2 j_2$ to a final state $v'_1 j'_1 v'_2 j'_2$ for $\text{H}_2\text{-H}_2$ and similarly for $\text{H}_2\text{-He}$. Thus, in order to keep the computational task at the elevated temperatures feasible, for most of the calculations we have employed the isotropic potential approximation (IPA) [1], which neglects the anisotropic terms of the intermolecular potential, even though they are available from our *ab initio* calculations. This uncouples the contributions from the 26 different spherical dipole components and makes the computational task possible. However, some calculations [14] were also carried out based on the new induced dipole surface and the close-coupled computer code [14–16], which takes into account the

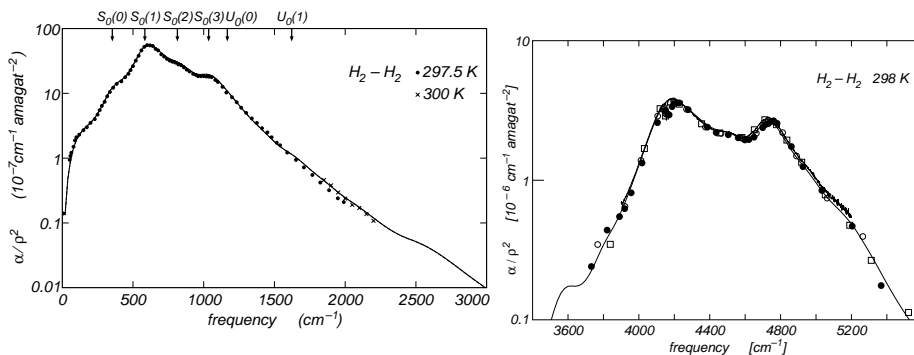


FIGURE 1. Left: Comparison of the calculated rototranslational absorption spectrum (solid curve) of H_2-H_2 with laboratory measurements (crosses from [17], dots from [18]), at 300 K. A dashed curve with an earlier well-established potential [1, 11] is also plotted on the left, but on this scale, it is virtually indistinguishable from the solid curve. Both show excellent agreement with the measurements. Right: CI absorption by pairs of H_2 molecules in hydrogen gas, fundamental band at room temperature. Calculation: solid smooth trace. Measurements: dots from [19], open circles from [20], filled squares from [21]; slightly noisy trace from [22].

anisotropy of the intermolecular potential.

RESULTS

The left side of Fig. 1 shows the calculated absorption coefficient $\alpha(\nu, T)$, normalized by the gas density ρ squared, at a temperature of 300 K, and frequencies ν from 0 to 3,000 cm^{-1} (the "rototranslational band"). Excellent agreement between the fundamental theory and the laboratory measurements [17, 18] is observed. Furthermore, for test purposes a calculation, based on an earlier well-established potential [1, 11], is shown. The two calculations agree well with each other. On the right side of Fig. 1 a comparison between the fundamental theory and measurements in the H_2 fundamental band is shown. The calculation agrees with the experimental data similarly well.

Similarly good agreement of theory and measurement was previously observed where absorption is strong, based on an earlier *ab initio* IDS and refined intermolecular potential [1, 11]. The IDS obtained in this work is more complete, although the extension has not significantly affected the regions of strong absorption in the rototranslational band near room temperature. However, it should be pointed out here that historically the absorption minima have been important for astrophysical applications, but could not be computed previously with the desired accuracy, because they are superpositions of a large number of very weak contributions to the absorption. These minima are shaped by higher-order spherical dipole components which are completely insignificant near the absorption peaks. This fact is related to the selection rules $j'_1 - j_1 = 0, \pm 2, \dots, \pm \lambda_1$, for the dipole component $D_{\lambda_1 \lambda_2 \Lambda L}$ with indices λ_1 for molecule 1, λ_2 for molecule 2, Λ for the coupling, and L for the intermolecular vector (and similarly for $j'_2 - j_2$). While the H_2 S lines are generated mainly by dipole components with λ_1 or $\lambda_2 = 2$, absorption near the minima arises significantly from higher-order dipole components ($\lambda_1 + \lambda_2 > 2$),

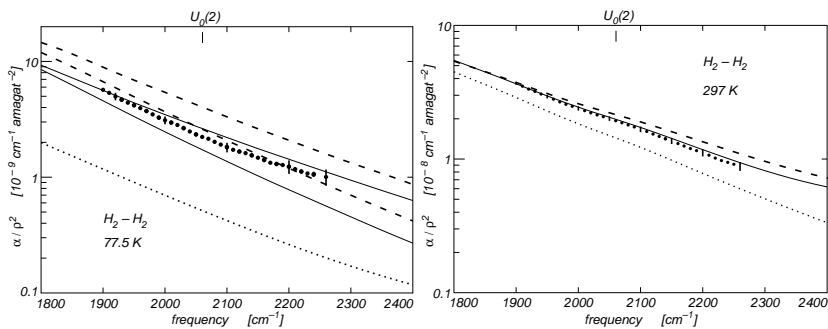


FIGURE 2. Left: absorption coefficient α of $\text{H}_2\text{-H}_2$ collisional complexes as function of frequency, normalized by the square of density ρ , near wavelengths of $5\mu\text{m}$, at a temperature of 77.5 K . Lower solid curve: calculation based on IPA and the new IDS. Upper solid curve: calculation based on the new IDS and close-coupled scattering theory, which accounts for the anisotropy of the interaction potential. Lower dashed curve: IPA calculation with previous IDS. Upper dashed curve: CC calculation with previous IDS (from [16]). Dotted curve: same as lower solid curve, except that the 0443+0445 and 4043+4045 dipole components are suppressed to demonstrate the significance of those dipole components, which were previously not well enough determined [14]. Dots: measurement from [16]. Right: similar comparison at room temperature. Solid curve: IPA calculation based on 25 induced dipole components. Dashed curve: IPA calculation with the previous eight dipole components ([11–13]). Dotted curve: same as solid curve, except that the 0443+0445 and 4043+4045 dipole components are suppressed to demonstrate the significance of those dipole components [14]. Dots: measurement from [16].

which were previously not well enough determined. As shown in Fig. 2 [14], with the new more complete IDS the measurements in the far blue wing of the rototranslational spectrum are now explained. In the previous IDS the $\lambda_1\lambda_2\Lambda L = 0443$ and 0445 and the $\lambda_1\lambda_2\Lambda L = 4043$ and 4045 dipole components were combined into effective values of the 0445 and 4045 components (with the 0443 and 4043 components set to zero). They do, however, have different dependences on the intermolecular separation. In our new IDS these components are appropriately separated so that the CI absorption can now be computed accurately.

Similarly good agreement between the fundamental theory and the laboratory measurements is seen in Fig. 3, which shows the CI absorption in the first overtone band of hydrogen and the fundamental band of deuterium, both at room temperature. Further comparisons with laboratory measurements and checks of the new IDS and PES are reported in [23] and will be published subsequently.

Having performed extensive checks of the new PES and IDS one may proceed to higher temperatures and frequencies where there are no laboratory measurements for comparison. Figure 4 shows the calculated binary CI absorption by hydrogen-helium mixtures at 600 K (left) and by molecular hydrogen pairs at 300 K and $2,000\text{ K}$ (right); also see the contribution by L. Frommhold *et al.* in this volume.

We are presently attempting calculations of $\text{H}_2\text{-H}_2$ opacities at still higher temperatures and frequencies. Moreover, similar calculations are in progress for $\text{D}_2\text{-D}_2$, $\text{H}_2\text{-He}$, $\text{D}_2\text{-He}$, and $\text{H}_2\text{-H}$ collisional complexes.

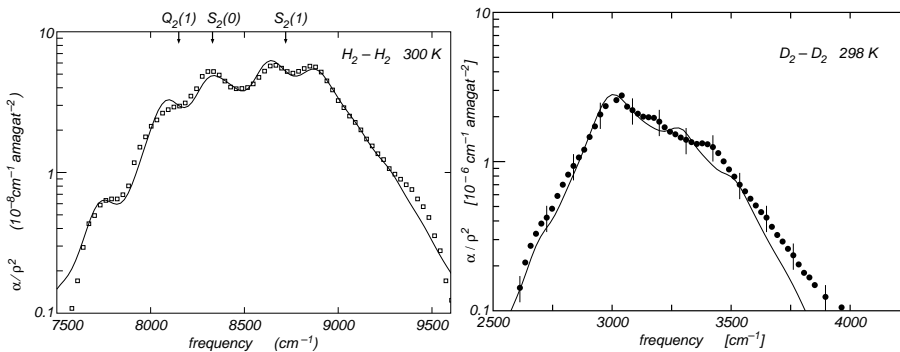


FIGURE 3. Left: CI absorption by pairs of H_2 molecules in the first overtone at room temperature. Calculation: solid trace. Measurement: squares from [24]. Right: CI absorption by pairs of D_2 in deuterium gas in the fundamental band at room temperature. Calculation: solid smooth trace. Measurement: dots from [25]. The error bars shown correspond to an estimated experimental uncertainty of 20 percent.

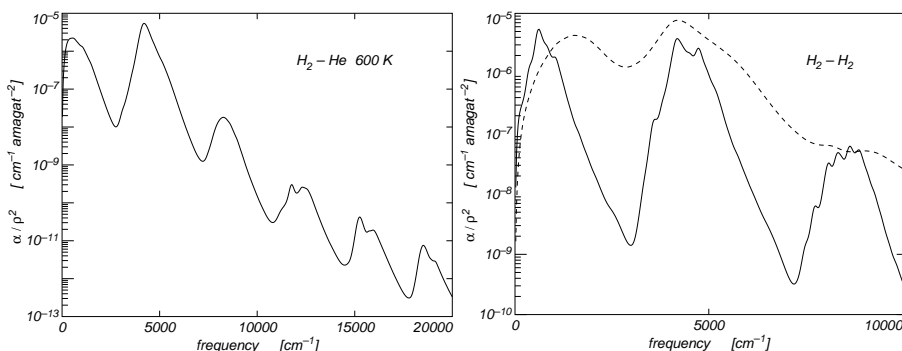


FIGURE 4. Calculated absorption spectrum of H_2 -He at 600 K (left) and of molecular hydrogen pairs at 300 K (solid curve) and at 2,000 K (dashed curve) (right). With increasing temperature the structures broaden substantially.

CONCLUSION

Opacity calculations of collisional H_2 - H_2 complexes have been carried out for temperatures of thousands of kelvin and frequencies from the microwave to the visible regions of the electromagnetic spectrum. In order to accurately take into account the rovibrational excitations of the involved molecules, new *ab initio* PES and IDS have been obtained, which are intended to facilitate modeling the atmospheres of cool stars. Agreement with earlier theoretical work and laboratory measurements, where these exist, is excellent. The new surfaces have been extensively tested so that the collision-induced opacities can be accurately calculated at the frequencies and temperatures where no laboratory measurements exist.

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