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Collision-induced absorption at temperatures of thousands of kelvin, from first principles, for astrophysical applications

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Abstract. New *ab initio* surfaces of the potential energies and the induced electric dipole moments of H₂–H₂ and H₂–He collisional complexes are obtained with H₂ bond distances from 0.942 to 2.801 bohr. These data permit the calculation of collision-induced absorption (CIA) spectra of dense hydrogen-helium gas mixtures at temperatures up to thousands of kelvin, *i.e.*, under conditions where strong rovibrational excitations of the H₂ molecules exist. First results of CIA spectra are obtained over an extended range of frequencies and temperatures. The work is an extension of our previous work on the opacities of the (low-temperature) atmospheres of the outer planets.

INTRODUCTION

So-called infrared inactive gases, *e.g.* hydrogen and hydrogen-helium gas mixtures, do absorb infrared radiation if gas densities are sufficiently high [1, 2]. In collisional interactions of two (or more) molecules electric dipole moments are induced by the same familiar mechanisms which cause the van der Waals forces: dispersion, electron exchange, and multipolar induction. Induced dipoles interact with electromagnetic radiation. The resulting collision-induced absorption (CIA) spectra usually appear as continua, extending at high temperatures from the microwave region to visible frequencies. The continua consist of a large number ($\sim 10^5$) of very diffuse, overlapping “lines” that arise from optical transitions, *e.g.*, for H₂–H₂ complexes, according to

$$|v_1 j_1 v_2 j_2\rangle + \hbar\omega \rightarrow |v'_1 j'_1 v'_2 j'_2\rangle. \quad (1)$$

The v and j are vibrational and rotational quantum numbers of two interacting hydrogen molecules (subscripts 1 and 2); a prime indicates the final state and $\hbar\omega$ stands for the absorbed photon. Averaging over the Maxwellian distribution of initial speeds is implied. The spectroscopically most significant intermolecular interactions occur in collisional encounters (free-to-free transitions of the collisional H₂–H₂ complex), but small contributions (especially at low temperatures < 300 K) are also present which involve van der Waals molecules, (H₂)₂ (bound-to-free, free-to-bound, bound-to-bound transitions). The extra-ordinary widths of these “lines” are related to the short duration of fly-by collisions ($\sim 10^{-13}$ s). Previous work of the kind provided opacity data for the

FIGURE 1. Four measurements of the emission spectrum of the cool white dwarf WD0346+246: solid squares and triangles, and traces in the visible (at short wavelengths λ) and infrared ($\lambda \geq 1 \mu\text{m}$) [3]. A blackbody spectrum at the temperature of 3850 K is also shown (thin solid line) for comparison, which roughly describes measurements at short wavelengths, but diverges strongly at the longer wavelengths.

outer planets, where temperatures and frequencies are low ($\ll 300 \text{ K}$ and far infrared frequencies [2]).

Our current interests are the atmospheric opacities of the oldest white dwarf stars and of other “cool” stars. White dwarfs are the remnants of main sequence stars such as the sun, after the supply of hydrogen is exhausted. In the subsequent cooling process the helium cores shrink to the point where electron degeneracy forces balance gravity. If the mass of the remnant is of the order of a solar mass (but not much greater), the resulting core densities are low enough to prevent helium from burning to ^{12}C and ^{16}O so that the cores are thought to simply and slowly cool down from roughly 150,000 K to eventually reach space temperature. However, the coolest (*i.e.*, oldest) white dwarfs that we know — and we know many hundreds — have core temperatures of roughly 4000 K, which is much higher than space temperature. This must mean that the universe is not old enough for the embers of the oldest stars to cool down to the much lower temperatures of space yet. Since the cooling process is conceptually very simple, cool white dwarfs may be considered clocks that have been ticking for many billions of years: knowledge of the core temperature permits the evaluation of the age of the core.

It has long been known that the atmospheres of cool white dwarf stars absorb strongly in the infrared [4, 5]. These atmospheres are mixtures of helium and hydrogen and, because neither H_2 molecules nor helium atoms are infrared active, the opacity must be due predominantly to supermolecular processes [6, 7], namely collision-induced absorption by $\text{H}_2\text{--X}$ collisional complexes, with $\text{X} = \text{H}_2$, He, or perhaps H. Figure 1 shows the spectrum of one of the oldest (*i.e.*, coolest) white dwarfs [3]. Whereas at wavelengths λ in the visible, blackbody curves of roughly 3850 K more or less reproduce the observed spectrum, in the infrared ($\lambda \geq 1 \mu\text{m}$) radiation from the core is strongly filtered: with increasing wavelengths the blackbody curve (thin line in Fig. 1)

FIGURE 2. Quantum chemical calculations of two H_2 molecules. The ϕ and θ are azimuthal and polar angles of molecule 1 (to the left) and 2 (right); R is the center-to-center separation; bond distances r_1 and r_2 over a range from 0.942 to 2.801 bohr are chosen.

departs more and more from the observed intensities, presumably due to CIA. Reliable opacity data for quantitative analyses are presently not available. The goal of this work is to provide data of $\text{H}_2\text{-X}$ opacities from first principles for conditions encountered in the atmospheres of cool white dwarfs.

CALCULATIONS

At temperatures of thousands of kelvin H_2 molecules are substantially rovibrationally excited; collision-induced absorption of a photon in the near infrared leads to even higher rovibrational excitation of one or both of the interacting molecules. For a calculation of the resulting opacities, new induced dipole and potential energy surfaces (IDS, PES) of $\text{H}_2\text{-H}_2$ and $\text{H}_2\text{-He}$ complexes were obtained by our associates at Michigan State University, using advanced quantum chemical methods [8, 9]. These computational methods had to be refined enough to model the weak van der Waals interactions well; they must also account for the strong rovibrational excitations of the interacting molecules. Once suitable IDS and PES are obtained for a given collisional system, molecular state to state scattering calculations are undertaken, where the collisional complex of two rovibrating molecules is coupled to the electromagnetic radiation field through the interaction-induced electric dipole moment. Such calculations provide the binary absorption spectra over a wide range of temperatures and frequencies of electromagnetic radiation. Computational results show close agreement of the computed absorption spectra with laboratory measurements where these exist; see the contribution by M. Abel *et al.* elsewhere in this volume.

Quantum chemical calculations

For H_2 pairs a basis set known as “aug-cc-pV5Z (spdf)” was used with MOLPRO2000 in a coupled cluster singles plus doubles plus perturbative triples (CCSD(T)) treatment [8, 9]. A similar set was used for $\text{H}_2\text{-He}$ complexes, which however also included g functions. For $\text{H}_2\text{-H}_2$ complexes 28 bondlengths combinations r_1 , r_2 were chosen from the set { 0.942, 1.111, 1.280, 1.449, 1.787, 2.125, 2.463, 2.801 bohr}. 17 independent

FIGURE 3. The $\text{H}_2\text{-H}_2$ dipole tensor component $A_{0223}(r_1, r_2, R)$ at $R = 4$ bohr.

geometries $\theta_1, \theta_2, \phi_2$ with $\phi_1 = 0$ were computed, Fig. 2. Supermolecular properties, such as the potential energy surface of $\text{H}_2\text{-H}_2$ complexes and the induced dipole surface, are obtained at seven separations, $R = 4, 5, 6, 7, 8, 9, 10$ bohr, with calculations of eight further separations, $R = 2, 2.2, 2.4, 2.6, 2.8, 3, 3.5, 4.5$ bohr presently in progress. For $\text{H}_2\text{-He}$ complexes, the PES and IDS are already available for the whole set of 15 separations.

Cartesian dipole components μ_x, μ_y, μ_z are obtained by the finite field method. These are then converted to spherical tensor components,

$$\begin{aligned}\mu_0 &= \mu_z \\ \mu_{\pm 1} &= \mp(\mu_x \pm i\mu_y)/\sqrt{2}\end{aligned}\quad (2)$$

and expanded in terms of the orientational parameters [10, 11],

$$\begin{aligned}\mu_M(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) &= \frac{(4\pi)^{\frac{3}{2}}}{\sqrt{3}} \sum A_{\lambda_1 \lambda_2 \Lambda L}(r_1, r_2, R) Y_{\lambda_1}^{m_1}(\mathbf{\Omega}_1) Y_{\lambda_2}^{m_2}(\mathbf{\Omega}_2) Y_L^M(\mathbf{\Omega}_R) \\ &\quad \times C(\lambda_1 \lambda_2 \Lambda, m_1 m_2 m) C(\Lambda L 1, m(M-m)M)\end{aligned}\quad (3)$$

The summation is over all $\lambda_1, \lambda_2, \Lambda, L, m_1, m_2, m$; the Y are spherical harmonics; the $\mathbf{\Omega} = \theta, \phi$ are the orientational angles of the intramolecular axes $\mathbf{r}_1, \mathbf{r}_2$; $\mathbf{R}$ is the vector separation of the collisional pair; the $C(\dots, \dots)$ are Clebsch-Gordan coefficients; and $M = 0, \pm 1$. The A coefficients are the spherical dipole tensor components (the “unknowns”), the solution of the system of equations (3) for the 17 different sets of orientations $\mathbf{\Omega}_1, \mathbf{\Omega}_2, \mathbf{\Omega}_R$.

For the $\text{H}_2\text{-H}_2$ complex, 11 tensor components A were determined with $\lambda_1 \lambda_2 \Lambda L = 0001, 0221, 0223, 2021, 2023, 2211, 2233, 0443, 0445, 4043, 4045$, along with several other higher-order components, which were seen to be negligible for our purpose. The most important dipole components are the A_{0223} , which describes basically the dipole induced *via* the trace of the polarizability tensor of molecule 1 by the electric field of the quadrupole moment of molecule 2, and A_{2023} where molecules 1 and 2 are exchanged.

FIGURE 4. The $\text{H}_2\text{-He}$ dipole tensor component A_{23} versus the H_2 bond length r , at the fixed intermolecular separation of $R = 3$ bohr.

Figure 3 shows as an example the former at the fixed intermolecular separation of $R = 4$ bohr.

An expression similar to Eq. (3) may be written down for the spherical dipole tensor components $A_{\Lambda L}(r, R)$ of $\text{H}_2\text{-He}$ collisional systems [2]. An example of the IDS obtained at fixed separation $R = 3$ bohr is shown in Fig. 4. We mention that one of the strongest induced dipole components is the one with the expansion parameters $\Lambda L = 23$, which arises mainly by polarization of the He atom in the electric quadrupole field of the H_2 molecule. Together with the isotropic A_{01} component these are the strongest induced dipole components of the $\text{H}_2\text{-He}$ complex.

Highly developed intermolecular potentials exist for many systems, including $\text{H}_2\text{-H}_2$ and $\text{H}_2\text{-He}$ complexes [12, 13]. For the present purposes these are, however, not well suited, because of the common neglect of the rovibrational state dependence of the molecules involved. “Effective” potentials have been proposed that are said to account for “average” rovibrational excitations under certain experimental conditions; see for example Ref. [14] for $\text{H}_2\text{-H}_2$. For state to state scattering calculations, effective potentials used on a trial basis were not very successful and we decided to use an *ab initio* potential energy surface which was obtained using quantum chemical computations [15]. The best computational potential models tend to give very accurate repulsive cores, but typically have some uncertainties in the well region, where empirical data are used to improve theoretical potential models when substantial rovibrational excitations do not occur, at low temperatures, say 300 K or so. Our present interest is CIA at high temperatures, up to thousands of kelvin. Under such conditions the well and long-range regions of the intermolecular potentials of $\text{H}_2\text{-H}_2$ and $\text{H}_2\text{-He}$ do not really matter as test calculations at 300 K have shown: CIA spectra of $\text{H}_2\text{-H}_2$, calculated with an advanced intermolecular potential and also with the new *ab initio* potential energy surface (PES) [15] are virtually indistinguishable, see M. Abel *et al.* elsewhere in this volume.

Several anisotropic components of the new PES for $\text{H}_2\text{-H}_2$ and $\text{H}_2\text{-He}$ are actually available, but we use the isotropic parts only. The accounting for the anisotropy for the scattering process is possible, but that would complicate the computational effort immensely. Moreover, previous work [2] has shown that, at least at temperatures of ≈ 300 K or less, the effects of the intermolecular anisotropy of the interaction is rather

FIGURE 5. The isotropic part $\mathcal{V}_{000}(r_1, r_2, R)$ of the $\text{H}_2\text{-H}_2$ potential energy surface at the intermolecular separation of $R = 4$ bohr.

FIGURE 6. The isotropic part $\mathcal{V}_{00}(r, R)$ of the $\text{H}_2\text{-He}$ potential energy surface at the fixed intermolecular separation of $R = 3$ bohr.

insignificant in those regions of the spectrum where absorption is strong; only in the deep absorption minima between the regions of strong absorption the effects of the anisotropy are discernible in the calculated spectra [16, 17]. Accounting of the anisotropy of the intermolecular interactions would require an enormous computational effort which we are not prepared to undertake at this point.

The isotropic parts $\mathcal{V}_{000}(r_1, r_2, R)$ and $\mathcal{V}_{00}(r, R)$, of the potential energy surfaces $\mathcal{V}$ of $\text{H}_2\text{-H}_2$ and $\text{H}_2\text{-He}$ at fixed intermolecular separations R are shown in Figs. 5 and 6, respectively. Potential energies change significantly with changes of the bond distances r . This fact suggests that the rotovibrational states, and changes of such states, affect the molecular interactions quite noticeably as was observed previously for even small vibrational excitations [2].

Molecular scattering calculations

Once the induced dipole surface and the potential energy surface are obtained for a given system, state to state molecular scattering calculations may be started. Energy

conservation in an optical transition of a collisional complex consisting of two H_2 molecules may be written as

$$\text{H}_2(v_1, j_1) + \text{H}_2(v_2, j_2) + \hbar\omega + \text{KE} \rightarrow \text{H}_2(v'_1, j'_1) + \text{H}_2(v'_2, j'_2) + \text{KE}' \quad (4)$$

where KE is the kinetic energy of relative motion of the collisional pair prior to the collision and KE' is the kinetic energy after the collision. The center frequency of the associated absorption line is given by the expression

$$\hbar\omega_{\text{ctr}} = (E(v'_1, j'_1) - E(v_1, j_1)) + (E(v'_2, j'_2) - E(v_2, j_2)) , \quad (5)$$

which is independent of the kinetic energies of the collisional encounter. The rotovibrational energy of the H_2 molecule is $E(v, j)$. An optical transition in a collisional complex may change the rotovibrational state in one or in both of the interacting molecules, depending on the symmetry of the spherical dipole component considered. A complete collision-induced absorption (CIA) spectrum consists of a large number ($\sim 10^6$) of such “lines”. Each line is very broad and overlaps with other such lines, owing to the short duration of a collision ($\sim 10^{-13}$ s) so that the resulting spectra appear as a somewhat structured continuum.

For the H_2 – H_2 complex the scattering hamiltonian $\mathcal{H}$ takes the form [18, 19, 20]

$$\mathcal{H} = \mathcal{H}_1(\mathbf{r}_1) + \mathcal{H}_2(\mathbf{r}_2) - \frac{\hbar^2}{2m} \nabla_{\mathbf{R}}^2 + \mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) - \boldsymbol{\mu}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) \cdot \mathbf{X} + \mathcal{H}^{\text{rad}}. \quad (6)$$

In this expression $\mathcal{H}_1$ and $\mathcal{H}_2$ are the rotovibrational hamiltonians of molecules 1 and 2, respectively; the third term to the right is the kinetic energy operator of relative motion; m is the reduced mass of the collisional system; $\mathcal{V}$ is the potential energy surface; $-\boldsymbol{\mu} \cdot \mathbf{X}$ couples the collisional pair to the radiation field $\mathbf{X}$ through the induced electric dipole moment $\boldsymbol{\mu}$; and $\mathcal{H}^{\text{rad}}$ is the radiation hamiltonian.

The $\boldsymbol{\mu} \cdot \mathbf{X}$ term is treated as a perturbation so that with an isotropic potential energy surface $\mathcal{V}_{000}(r_1, r_2, R)$ the radial scattering hamiltonian after some manipulations reduces to the simple form [2]

$$\mathcal{H}(R) = -\frac{\hbar^2}{2mR^2} \frac{d}{dR} \left(R^2 \frac{d}{dR} \right) + V_{000}^c(R) + \frac{\hbar^2 \ell(\ell+1)}{2mR^2} \quad (7)$$

with

$$V_{000}^c(R) = \langle v_1 j_1 v_2 j_2 | \mathcal{V}_{000}(r_1, r_2, R) | v_1 j_1 v_2 j_2 \rangle \quad (8)$$

for the initial state, and similarly for the final (primed) state. The superscript c to the left of Eq. (8) is short for the set of the rotovibrational quantum numbers $v_1 j_1 v_2 j_2$. Associated radial scattering wave functions $\psi_{\ell k}^c(R)$ must be computed numerically.

Equation (8) shows how the intermolecular potentials are related to the theoretical PES $\mathcal{V}$. It is interesting to compare the resulting intermolecular potentials $V(R)$ for H_2 molecules in the rotovibrational ground state with existing refined potential models, Figs. 7 and 8, respectively. The current intermolecular potential for H_2 – H_2 complexes compares well with an advanced semi-empirical model [21] at separations from $R = 4$ to almost 6 bohr; at the shorter separations R presently no new data are available but

FIGURE 7. Isotropic intermolecular potential of H_2 pairs if both H_2 molecules are in the rovibrational ground state ($v_1 = j_1 = v_2 = j_2 = 0$; solid line); ditto: dashed line, except that $v_1 = 5$ and $j_1 = v_2 = j_2 = 0$. For comparison, an advanced semi-empirical H_2 – H_2 potential [21] is also shown where both molecules are in the rovibrational ground state (circles).

are forthcoming. A simple exponential extrapolation for small $R < 4$ bohr is employed which presently limits the validity of our high temperature data (somewhere between 2000 and 3000 K). We note that for larger $R > 6$ bohr, the deviations of our potential from the refined model are small enough to be indiscernible in a comparison of the spectra computed with both potentials; see M. Abel *et al.* elsewhere in this volume.

Figure 8 compares similarly the present intermolecular potential of H_2 in the rovibrational ground state, interacting with atomic He, with an earlier *ab initio* potential of high quality [22]. For the H_2 –He complex we have new results for the potential and the collision-induced dipole over the full range of R values accessible at high temperatures. The comparison with the earlier *ab initio* potential [22] is very good for the presently important separations $R < 5$ bohr. A discernibly different interaction potential is obtained if the H_2 molecule is in the $v = 5, j = 0$ state (dashed).

Profiles of individual lines are computed according to [2]

$$V G_s^{c'c}(\bar{\omega}, T) = \lambda_0^3 \hbar \sum_{\ell \ell'} (2\ell + 1) C(\ell L \ell'; 000)^2 \int_0^\infty e^{-\frac{\hbar^2 k^2}{2m\kappa T}} \left| \langle \ell k | B_s^{c'c}(R) | \ell' k' \rangle \right| dk \quad (9)$$

where we have used κ to denote Boltzmann's constant, k is the magnitude of the wave vector associated with the momentum of the colliding molecules and $B_s^{c'c}(R)$ is the induced dipole operator,

$$B_s^{c'c}(R) = \langle v'_1 j'_1 v'_2 j'_2 | A_{\lambda_1 \lambda_2 \Lambda L}(r_1, r_2, R) | v_1 j_1 v_2 j_2 \rangle ; \quad (10)$$

s is short for the individual members of the set of expansion coefficients $\lambda_1 \lambda_2 \Lambda L$. The kinetic energy of relative motion of the two molecules equals $\hbar^2 k^2 / 2m$ and the frequency

FIGURE 8. Isotropic intermolecular potential of $\text{H}_2\text{-He}$ complexes if the H_2 molecule is in the rovibrational ground state (solid line); ditto: the H_2 molecule is vibrationally excited ($v = 5, j = 0$; dashed line). For comparison the earlier *ab initio* $\text{H}_2\text{-He}$ potential [22] is also shown (dotted line) where the H_2 molecule is in its rovibrational ground state.

shift $\bar{\omega}$ is given by

$$\hbar\bar{\omega} = \hbar^2 ((k')^2 - k^2) / 2m. \quad (11)$$

The binary absorption coefficient α of hydrogen is then given by [2]

$$\alpha(\omega, T) = \frac{2\pi^2 N_a^2}{3\hbar c} \rho^2 \omega \left(1 - e^{-\frac{\hbar\omega}{kT}}\right) V g(\omega, T) \quad (12)$$

with

$$V g(\omega, T) = \sum_s \sum_{c'c} (2j_1 + 1) P_1(T) C(j_1 \lambda_1 j_1'; 000)^2 (2j_2 + 1) P_2(T) C(j_2 \lambda_2 j_2'; 000)^2 \times V G_s^{c'c}(\omega - \omega_{c'c}, T) \quad (13)$$

Here $N_a = 2.69 \times 10^{19} \text{ cm}^{-3}$ is the Loschmidt number; ρ is the density of the gas in amagat units; P_1 and P_2 are rovibrational Boltzmann factors of the molecules; ω is 2π times the absolute frequency. Similar expressions as in Eqs. (9) through (13) may be written down for hydrogen-helium mixtures [2].

THE SPECTRA

Figure 9 shows the computed binary collision-induced absorption spectrum of hydrogen-helium complexes. Peak absorption is at low frequencies near 4200 cm^{-1} and amounts to $\approx 5 \cdot 10^{-5} \text{ cm}^{-1}$ at standard pressure ($\rho_1 = \rho_2 \approx 1$ amagat), which corresponds to a mean absorption path length of 20,000 cm. The mean absorption path length decreases

FIGURE 9. The calculated absorption coefficient $\alpha(\omega, T)$ as function of angular frequency $\omega = 2\pi f$ and temperature $T = 300$ K, divided by the product of the (numerical) densities ρ_1 and ρ_2 of hydrogen and helium, respectively.

FIGURE 10. The calculated absorption coefficient $\alpha(\omega, T)$ as function of angular frequency $\omega = 2\pi f$ and temperatures T from 300 to 3000 K, divided by the (numerical) density squared (ρ^2), of dense hydrogen gas.

as $(\rho_1 \rho_2)^{-2}$ with increasing gas density. It decreases also with increasing frequency (but not monotonically). The spectrum shows several broad peaks and deep minima between them. The peaks correspond roughly to the pure rotational spectrum of H_2 to the left, followed by the fundamental band and the first, second, third, and fourth overtones of H_2 — all of which are of course dipole-forbidden in the non-interacting H_2 molecule. The small structures near the peaks are mostly (very broad!) H_2 $S_V(j)$ lines, *i.e.*, lines with $\Delta j = 2$, which arise primarily from quadrupolar induction as mentioned above.

For H_2 - H_2 complexes a similar spectrum exists [8]. With increasing temperatures, the

coarse structures seen at low temperatures (~ 300 K) in Figs. 9 and 10 broaden substantially and the interband minima get less and less pronounced; at the highest temperatures the absorption spectrum appears rather unstructured, Fig. 10. This is plausible because with increasing temperature the individual “lines” broaden substantially. Moreover, with increasing temperature the initial states of the collisional complexes are likely to be ro-vibrationally excited so that many more optical transitions with different frequencies open up over the whole range of frequencies.

In conclusion we mention that at the present time the $\text{H}_2\text{-H}_2$ spectral line shape calculations are limited to temperatures below 3000 K and frequencies below $10,000\text{ cm}^{-1}$, due to the absence of induced dipole and potential data at small separations (< 4 bohr). Efforts to calculate the necessary data and to supplement the presently insufficient data are underway.

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