Raman spectra of hydrocarbons under extreme conditions of pressure and temperature: a first-principles study

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Abstract

Hydrocarbons are of great importance in carbon-bearing fluids in deep Earth and in ice giant planets at extreme pressure (P)–temperature (T) conditions. Raman spectroscopy is a powerful tool to study the chemical speciation of hydrocarbons. However, it is challenging interpreting Raman data at extreme conditions. Here, we performed ab initio molecular dynamics simulations coupled with the modern theory of polarization to calculate Raman spectra of methane, ethane and propane up to 48 GPa and 2000 K. Our method includes anharmonic temperature effects. We studied the pressure and temperature effects on the Raman bands and identified the characteristic Raman modes for the C–C and C–C–C bonds. To the best of our knowledge, this is the first time that the Raman spectra of hydrocarbons have been calculated at extreme P–T conditions. Our results may help with the interpretation of in situ Raman data of hydrocarbons at extreme P–T conditions, with important implications for studying hydrocarbon reactions in the deep carbon cycle inside Earth and the composition of ice giant planets.

Supplementary material for this article is available online

Keywords: first-principles method, Raman spectroscopy, ab initio molecular dynamics, density functional perturbation theory, hydrocarbons

(Some figures may appear in colour only in the online journal)

1. Introduction

Methane (CH₄) and other light hydrocarbons are important components of reduced carbon–hydrogen–oxygen (C–H–O) fluids inside deep Earth [1, 2]. Methane is also a major constituent of the deep interiors of two ice giant planets in the Solar System: Uranus and Neptune [3, 4]. Although in the scientific community, it is more widely accepted that petroleum, as a fossil fuel, was formed from sedimentary organisms, such as zooplankton and algae, by organic means, the abiotic hydrocarbons may also participate in the formation of petroleum deposits [5]. This controversial hypothesis can be dated back to the time of Dimitri Mendeleev [2, 6]. The properties of hydrocarbons under extreme pressure (P) and temperature (T) conditions play crucial roles in the deep carbon cycle in the Earth [2], and in shaping the structure and dynamics of ice giant planets. Previously, it was assumed that hydrocarbons were simply mixed with other small volatile molecules, e.g. H₂O, CO₂, H₂, in C–H–O fluids [7] or with H₂O and NH₃ inside Uranus and Neptune [4]. However, many recent theoretical and experimental studies show that methane and other
hydrocarbons may further react under extreme P–T conditions (e.g. [8–13]). Using ab initio molecular dynamics (AIMD) simulations, Ancilotto et al found that at 100 GPa and 4000 K, methane dissociates into a mixture of methane, ethane (C\(_2\)H\(_6\)) and propane (C\(_3\)H\(_8\)) [8]. Spanu et al predicted that higher hydrocarbons become thermodynamically more favored than methane at above 4 GPa and 1000–2000 K [12]. Experiments with laser-heated diamond anvil cells reported that ethane, propane and higher hydrocarbons may form out of methane at pressures higher than 2 GPa and temperatures above 1000 K [9, 10].

Raman spectroscopy is one of the most widely used experimental tools to detect chemical speciation in C–H–O fluids under both high-P and high-T conditions [14]. Raman spectra of vibrations provide fingerprints to identify molecules and ions in in situ experiments [14, 15], so Raman spectroscopy can be used to monitor hydrocarbon reactions in C–H–O fluids at the molecular scale [16]. However, it is difficult to maintain high P and high T in experiments, and it is also very challenging to interpret Raman spectra under extreme P–T conditions because many high energy levels are excited at high temperatures and there may be interference from the signals from diamond anvils. For example, the peaks near 1332 and 2400 cm\(^{-1}\) are attributed to the first- and the second-order scattering from diamond anvils, respectively [17]. The experimental data under extreme P–T conditions are far fewer than those under ambient conditions. Pressure and temperature change the position and shape of Raman bands of hydrocarbons. Theoretically studying the P–T dependence of Raman modes is of great importance for the interpretation of Raman spectra under extreme conditions [13, 18]. Some theoretical studies using model Hamiltonians may give very accurate vibrational frequencies of small molecules compared with experiments, e.g. in [19, 20]. However, these models rely on high-quality experimental data to fit the parameters, and it is unknown if the fitted Hamiltonians can work outside the P–T range of experimental data, particularly when hydrocarbons transform from gas to supercritical fluid. Among various theoretical models, first-principles simulations have become increasingly popular in recent years to study material properties under extreme conditions because they directly apply fundamental laws of quantum mechanics to make reliable predictions, and do not need any experimental input [21]. For example, AIMD simulations predict that methane may dissociate to become diamond under extreme P–T conditions [8], which was later confirmed by experiments [22]. Ramya et al calculated and analyzed the Raman modes of methane clathrate hydrates using density functional theory (DFT) [23]. Lin et al applied first-principles calculations to obtain the Raman spectra of solid methane at high pressure and found that typical Raman active modes are in very good agreement with experimental data [24]. For the gas or solid phase, we usually calculate the change in electronic polarizability along a normal vibrational mode under a harmonic assumption to obtain the Raman spectra of hydrocarbons (e.g. [23, 24]), where the temperature is treated as 0 K. However, for C–H fluids at the supercritical state, temperature and anharmonic effects cannot be ignored [16, 25, 26]. Using AIMD, Putrino and Parrinello calculated the Raman spectra of high-pressure ice [25], and Wan et al obtained the Raman spectra of water under ambient conditions [26]. However, the Raman scattering of hydrocarbons in the supercritical state has not been studied theoretically, and it is not clear how pressure and temperature change Raman bands under extreme P–T conditions.

Here, we performed AIMD simulations coupled with density functional perturbation theory (DFPT) to calculate the Raman spectra of methane, ethane and propane at 13.4–48 GPa and 1445–2000 K. The electronic polarizability was calculated on-the-fly along with AIMD simulations. We studied how pressure and temperature affect Raman spectra and assigned Raman bands at the molecular scale. We discussed possible characteristic Raman signals for the formation of higher hydrocarbons. Our work has important implications for studying the chemical speciation of hydrocarbons under extreme P–T conditions found in deep Earth and ice giant planets.

2. Methods

We carried out AIMD simulations using the Qbox package [27, 28] with the Born–Oppenheimer approximation and a time step of 5 a.u. We used the Perdew–Burke–Ernzerhof (PBE) exchange-correlation (xc) functional [29] and the HSCV norm-conserving pseudopotentials [30–32] in the DFT calculations. The kinetic energy cutoff of the plane waves is 65 Ry, which was increased to 145 Ry to calculate the pressure. We applied the Bussi–Donadio–Parrinello thermostat to control temperature [33]. For methane, ethane and propane, the simulation boxes with periodic boundary conditions contain 56, 32 and 23 molecules, respectively.

We performed on-the-fly calculations, using DFPT [34] implemented in the Qbox package along with AIMD simulations to calculate the electronic polarizability, which were conducted every 25 MD steps after about 10 ps equilibration. Each MD trajectory is longer than 130 ps. We computed Raman spectra of supercritical fluids using the Fourier transform of the autocorrelation functions of polarizabilities. The isotropic and anisotropic Raman spectra are calculated respectively by

\[ R_{\text{iso}}(\omega) \propto \frac{\hbar \omega}{k_B T} \int dt e^{-i\omega t} \frac{\langle \alpha(0)\alpha(t) \rangle}{\langle \alpha(0)\alpha(0) \rangle}, \]

and

\[ R_{\text{aniso}}(\omega) \propto \frac{2}{15} \frac{\hbar \omega}{k_B T} \int dt e^{-i\omega t} \frac{\text{Tr}(\beta(0)\beta(t))}{\text{Tr}(\beta(0)\beta(0))}, \]

where \( \hbar \) is the Planck constant, \( \omega \) is the Raman frequency, \( k_B \) is the Boltzmann constant and \( \text{Tr} \) stands for the trace of the matrix. \( \alpha \) and \( \beta \) denote the isotropic and anisotropic components of the polarizability tensor, \( \alpha_{ij} = \frac{1}{3} \text{Tr} \alpha_{ij} \) and \( \beta_{ij} = \alpha_{ij} - \alpha_{il} \delta_{lj} \), respectively. In high-P and high-T experiments, we measured
unpolarized Raman spectra, which are obtained from a linear combination of equations (1) and (2):

\[ R_{\text{unpol}} = R_{\text{iso}} + \frac{7}{4} R_{\text{aniso}}. \]  

(3)

We further smoothed the Raman spectra using Gaussian broadening, whose full width at half maximum is 25 cm\(^{-1}\).

For the gas and solid phases, DFPT calculations were carried out using the Quantum Espresso package [35]. For methane, ethane and propane in the gas phase, the mean absolute error of calculated Raman frequencies is 22 cm\(^{-1}\) compared to the experimental values in Shimanouchi’s tables [36], and 30 cm\(^{-1}\) compared with Magnotti et al’s measurements [37] (see table S1 in the supporting information (available online at stacks.iop.org/JPD/55/044003/mmedia)). For crystal methane with P2\(_1/c\) symmetry at 48 GPa, the mean absolute error (MAE) between our Raman frequencies and Lin et al’s calculated results is 1.0 cm\(^{-1}\) [24]. Compared to Hirai et al’s experimental data, the MAE is 2.2 cm\(^{-1}\) for the modes at 3306, 3319, 3367, 3392 cm\(^{-1}\) (see figure S1 in the supporting information) [38]. The PBE xc functional seems to work better at high pressure than under ambient conditions, which is consistent with previous findings for the equation of state and the dielectric constant of water [39, 40]. The frequency accuracy may be further improved by using a high level of theory, e.g. a hybrid xc functional [41], but the computational cost will be very high when combined with AIMD simulations.

3. Results and discussion

Figure 1 shows the mean squared displacements of methane, ethane and propane at 13.4 GPa, 1445 K; 48 GPa, 1445 K; and 48 GPa, 2000 K. All the alkanes are in the supercritical state, except methane at 48 GPa and 1445 K, which is an amorphous solid. It is interesting to see that methane freezes at 1445 K, whereas propane does not. At ambient pressure, the melting point of methane is 90.7 K, while propane melts at 85.5 K [42]. In fact, the melting point of propane is unusually lower than that of other n-alkanes, which may be due to the low packing efficiency of propane molecules [42].

In our simulations, a few C–H bonds broke temporarily, but we did not see any new chemical bond form. Experimentally, Nellis et al reported no chemical reactions in shock wave experiments up to 26 GPa and 3200 K [43], whereas Lobanov et al found that heavier alkanes and unsaturated hydrocarbons may form in laser-heated diamond anvil cells above 1500 K [13]. Theoretically, Spanu et al found that mixtures of higher hydrocarbons and hydrogen become thermodynamically more stable than methane at above 4 GPa and 1000–2000 K using AIMD simulations and free-energy calculations, but without metal catalysts or unsaturated diamond surfaces they did not see chemical reactions in that P–T range [12]. Thus, we conclude that activation barriers of alkanes may be too high, and consequently, we could not see chemical reactivity within limited simulation time.

Figure 2 shows the unpolarized Raman spectra of hydrocarbons, from which we know how Raman bands change with pressure and temperature. The C–H bond stretching region is between 2800 and 3200 cm\(^{-1}\). The stretching band downshifts with increasing temperature or decreasing pressure. For methane at 48 GPa and 1445~2000 K, the stretching band splits into two peaks, which was found to be an indicator of orientational ordering of molecules in compressed methane crystals at least up to 30 GPa [44, 45], suggesting that CH\(_4\) molecules may have some orientational correlation under such extreme P–T conditions.

Figure 3 shows the angle distribution of two C–H bonds, respectively, from two nearest methane molecules. For the crystalline methane (space group: P2\(_1/c\) [24]), the angle distribution has two main peaks at 70.5° and 109.5°, and the former peak is taller than the latter. In the gas phase, the angle is randomly distributed, so the probability density function is \(\frac{\pi}{360°} \sin \theta\). At 48 GPa and 2000 K, the angle distribution
respectively: \( \nu_{\text{CH}} \) appears at \( ~1505 \text{ cm}^{-1} \). For an isolated methane molecule, the calculated Raman active mode in this range upshifts with increasing temperature. For an isolated ethane molecule, there are two notable Raman modes in our calculation: \( \nu_3 \) at 987 cm\(^{-1} \) and \( \nu_8 \) at 1455 cm\(^{-1} \), corresponding to the C–C stretching and CH\(_3\) degenerate deformation modes, respectively [36]. At 48 GPa and 1445 K, both of the peaks upshift. In addition to the C–H bond and H–C–H angle spectra, we also calculated the C–C bond spectrum:

\[
A_{\text{CC}}(w) = \int dt e^{-iwt} \left< \hat{\delta}_{\text{CC}}(0) \hat{\delta}_{\text{CC}}(t) \right> \left< \hat{\delta}_{\text{CC}}(0) \hat{\delta}_{\text{CC}}(0) \right>,
\]

where \( d_{\text{CC}} \) is the C–C bond length and \( \theta_{\text{HCH}} \) is the H–C–H bond angle. As shown in figure 4(A), there is no C–C stretching mode between 1000–1800 cm\(^{-1} \). The H–C–H angle spectrum has two peaks: \( \nu_4 \) at 1269 cm\(^{-1} \) and \( \nu_2 \) at 1511 cm\(^{-1} \). We cannot identify the \( \nu_4 \) mode in the calculated Raman spectrum in figure 4(A), because the Raman cross-section of \( \nu_2 \) is about 28 times that of \( \nu_4 \) for an isolated CH\(_4\) molecule.

Figure 4(B) shows the Raman spectra of ethane between 800–1800 cm\(^{-1} \). For an isolated ethane molecule, there are two notable Raman modes in our calculation: \( \nu_3 \) at 987 cm\(^{-1} \) and \( \nu_8 \) at 1455 cm\(^{-1} \), corresponding to the C–C stretching and CH\(_3\) degenerate deformation modes, respectively [36]. At 48 GPa and 1445 K, both of the peaks upshift. In addition to the C–H bond and H–C–H angle spectra, we also calculated the C–C bond spectrum:

\[
A_{\text{CC}}(w) = \int dt e^{-iwt} \left< \hat{\delta}_{\text{CC}}(0) \hat{\delta}_{\text{CC}}(t) \right> \left< \hat{\delta}_{\text{CC}}(0) \hat{\delta}_{\text{CC}}(0) \right>,
\]

where \( d_{\text{CC}} \) is the C–C bond length. It has a main peak at 1145 cm\(^{-1} \), which overlaps with the \( \nu_3 \) band, indicating that the \( \nu_3 \) mode is indeed the C–C stretching mode. The \( \nu_8 \) mode is found in the vicinity of the H–C–H angle spectrum, suggesting that the CH\(_3\) degenerate deformation is relevant to the variation of H–C–H angles. Comparing figure 4(A) to (B), we found that the \( \nu_3 \) band of methane overlaps with the \( \nu_8 \) band of ethane, and the \( \nu_5 \) band of ethane is missing in the Raman spectra of methane. Consequently, this band can be used as a characteristic signal for C–C bond formation under high P–T conditions. The \( \nu_3 \) mode upshifts with increasing pressure, and downshifts with increasing temperature. The pressure effect is more obvious than the temperature effect in the P–T range studied here, as shown in figure 2.

Figure 4(C) shows the Raman spectrum of propane between 800–1800 cm\(^{-1} \). In our calculation, an isolated propane molecule has notable Raman modes as follows: C–C stretching mode \( \nu_8 \) at 860 cm\(^{-1} \), C–C stretching mode \( \nu_12 \) at 1048 cm\(^{-1} \), CH\(_3\) rocking mode \( \nu_7 \) at 1137 cm\(^{-1} \), CH\(_2\) twisting mode \( \nu_13 \) at 1274 cm\(^{-1} \), and CH\(_3\) degenerate deformation mode \( \nu_{11} \) at 1435 cm\(^{-1} \) [36]. At 48 GPa and 1445 K, we can identify the \( \nu_12 \) and \( \nu_11 \) modes in the H–C–H angle spectrum. The C–C bond spectrum has three peaks: \( \nu_8 \), \( \nu_20 \) and \( \nu_7 \). We also calculated the C–C–C angle (\( \theta_{\text{CCC}} \)) spectrum:

\[
A_{\text{CCC}}(w) = \int dt e^{-iwt} \left< \hat{\theta}_{\text{CCC}}(0) \hat{\theta}_{\text{CCC}}(t) \right> \left< \hat{\theta}_{\text{CCC}}(0) \hat{\theta}_{\text{CCC}}(0) \right>,
\]

which has one peak overlapping with the \( \nu_{20} \) mode, indicating that this C–C stretching mode also considerably changes the C–C–C bond angle. The \( \nu_8 \) band does not show up in the spectra of methane and ethane, so it can be used to verify the formation of the C–C–C bonds.
We further divided Raman spectra into inter- and intramolecular contributions with the help of maximally localized Wannier functions [47], which provide local molecular orbitals to partition the electron density into molecules [48]. The effective molecular polarizability, $\alpha_{\text{mol}}^{\text{eff}}$, was obtained by,

$$\alpha_{\text{mol}}^{\text{eff}} \approx -e \int \mathbf{E} \Delta \rho_{\text{mol}} \, d\mathbf{r}, \quad (8)$$

where $\mathbf{E}$ is the macroscopic electric field, $e$ is the elementary charge, $\Delta \rho_{\text{mol}}$ is the electron polarization density of the molecule induced by the electric field, and the integral over the whole simulation box ($\Omega$).

The autocorrelation functions in equations (1) and (2) are respectively written as,

$$\langle \bar{\alpha}(0) \bar{\alpha}(t) \rangle = \left\langle \sum_{m=1}^{N_{\text{mol}}} \sum_{n=1}^{N_{\text{mol}}} \bar{\alpha}_{\text{mol},m}^{\text{eff}}(0) \bar{\alpha}_{\text{mol},n}^{\text{eff}}(t) + \sum_{m=1}^{N_{\text{mol}}} \left( \alpha_{\text{mol},m}^{\text{eff}}(0) \alpha_{\text{mol},m}^{\text{eff}}(t) \right) \right\rangle, \quad (9)$$

where $N_{\text{mol}}$ is the total number of hydrocarbon molecules. We applied the Fourier transform on the first and second terms of equations (9) and (10) to obtain the inter- and intramolecular Raman spectra, respectively.

Figure 5 shows the inter- and intramolecular Raman spectra in the high-frequency region. The intensity of the intermolecular contributions is much larger than the intramolecular ones, indicating strong molecular interactions under extreme P–T conditions. The intramolecular spectra have only one main peak, whereas there appear to be a few peaks in the intermolecular spectra, which may come from multiple intermolecular couplings between hydrocarbon molecules.
4. Conclusion

In summary, we calculated the unpolarized Raman spectra of methane, ethane and propane at 13.4–48 GPa and 1445–2000 K using AIMD simulations coupled with DFPT. Our method considers the Raman selection rule and anharmonic temperature effects. We monitored how pressure and temperature change the Raman bands, and understood the Raman bands at the molecular scale. In particular, we identified the characteristic Raman bands for the formation of C–C and C–C–C bonds. We found that the C–H stretching bands of supercritical hydrocarbons in the high-frequency region split due to the intermolecular interactions. Our results may help with the interpretation of the in situ Raman measurements of hydrocarbon reactions under extreme P–T conditions.

Hydrocarbons are an important carbon carrier in deep Earth and ice giant planets, so our study is of great importance in understanding the deep carbon cycle inside the Earth and the composition of ice giant planets.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Qbox is a free and open-source code available at http://qboxcode.org. Data processing scripts are available upon request from the authors.

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References

[1] Manning C E, Shook E L and Sverjensky D A 2013 The chemistry of carbon in aqueous fluids at crustal and upper-mantle conditions: experimental and theoretical constraints Rev. Mineral. Geochem. 75 109–48
[2] Septon M A and Hazen R M 2013 On the origins of deep hydrocarbons Rev. Mineral. Geochem. 75 449–65
[3] Hubbard W B 1981 Interiors of the giant planets Science 214 145–9
[4] Podolak M, Weizman A and Marley M 1995 Comparative models of Uranus and Neptune Planet. Space Sci. 43 1517–22
[5] McCollom T M 2013 Laboratory simulations of abiotic hydrocarbon formation in Earth’s deep subsurface Rev. Mineral. Geochem. 75 467–94
[6] Mendeleev D 1877 L’origine du pétrole Rev. Sci. 8 409–16
[7] Zhang C and Duan Z 2009 A model for C–O–H fluid in the Earth’s mantle Geochim. Cosmochim. Acta 73 2089–102
[8] Ancilotto F, Chiarotti G L, Scandolo S and Tosatti E 1997 Dissociation of methane into hydrocarbons at extreme (planetary) pressure and temperature Science 275 1288–90
[9] Hirai H, Konagai K, Kawamura T, Yamamoto Y and Yagi T 2009 Polymerization and diamond formation from melting methane and their implications in ice layer of giant planets Phys. Earth Planet. Inter. 174 242–6
[10] Kolesniov A, Kuchtero V G and Goncharov A F 2009 Methane-derived hydrocarbons produced under upper-mantle conditions Nat. Geosci. 2 566–70
[11] Gao G, Oganov A R, Mao H-K and Goncharov A F 2013 Carbon precipitation from methane under high pressure J. Chem. Phys. 133 144508
[12] Spanu L, Donadio D, Hohl D, Schweger E and Galli G 2011 Stability of hydrocarbons at deep Earth pressures and temperatures Proc. Natl Acad. Sci. USA 108 6843–6
[13] Lobanov S S, Chen P-N, Chen X-J, Zha C-S, Litasov K D, Mao H-K and Goncharov A F 2013 Carbon precipitation from heavy hydrocarbon fluid in deep planetary interiors Nat. Commun. 4 2446
[14] Goncharov A F 2012 Raman spectroscopy at high pressures Int. J. Spectrosc. 2012 617528
[15] Vandenabeele P 2013 Theoretical aspects Practical Raman Spectroscopy: An Introduction (New York: Wiley) pp 1–38
[16] Pan D and Galli G 2020 A first principles method to determine speciation of carbonates in supercritical water Nat. Commun. 11 421
[17] Goncharov A F, Goldman N, Fried L E, Crowhurst J C, Kuo I-F W, Mundy C J and Zaug J M 2005 Dynamic ionization of water under extreme conditions Phys. Rev. Lett. 94 125508
[18] Petrov D V 2018 Raman spectrum of ethane in methane environment J. Raman Spectrosc. 49 771–4
[19] Nikitin A V, Boudon V, Wenger C, Albert S, Brown L R, Bauerecker S and Quack M 2013 High resolution Raman spectroscopy and the first global analysis of the tetradecad
region of methane $^{12}\text{CH}_4$ Phys. Chem. Chem. Phys. 15 10071–93

[20] Amyay B, Louviot M, Pirali O, Georges R, Auwera J V and Boudon V 2016 Global analysis of the high temperature infrared emission spectrum of $^{13}\text{CH}_4$ in the dyad $(\nu_2/\nu_3)$ region J. Chem. Phys. 144 024312

[21] Gygi F and Galli G 2005 $ab$ initio simulation in extreme conditions Mater. Today 8 26–32

[22] Benedetti L R, Nguyen J H, Caldwell W A, Liu H, Kruger M and Jeanloz R 1999 Dissociation of CH$_4$ at high pressures and temperatures: diamond formation in giant planet interiors? Science 286 100–2

[23] Ramya K R, Pavan Kumar G V and Venkatakrishnan A 2012 Raman spectra of vibrational and librational modes in methane clathrate hydrates using density functional theory J. Chem. Phys. 136 174305

[24] Lin H, Li Y-ling, Zeng Z, Chen X-jia and Lin H Q 2011 Structural, electronic and dynamical properties of methane under high pressure J. Chem. Phys. 134 064515

[25] Putrino A and Parrinello M 2002 Anharmonic Raman spectra in high-pressure ice from ab initio simulations Phys. Rev. Lett. 88 176401

[26] Wan Q, Spanu L, Galli G A and Gygi F 2013 Raman spectra of liquid water from ab initio molecular dynamics: vibrational signatures of charge fluctuations in the hydrogen bond network J. Chem. Theory Comput. 9 4124–30

[27] Gygi F 2008 Architecture of Qbox: a scalable first-principles molecular dynamics code IBM J. Res. Dev. 52 137–44

[28] Gygi F (Available at: http://qboxcode.org/)

[29] Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865

[30] Hamann D R, Schlüter M and Chiang C 1979 Norm-conserving pseudopotentials Phys. Rev. Lett. 43 1494

[31] Vanderbilt D 1985 Optimally smooth norm-conserving pseudopotentials Phys. Rev. B 32 8412

[32] Gygi F Pseudopotential table (Available at: http://fpmd.ucdavis.edu/potentials/)

[33] Bussi G, Donadio D and Parrinello M 2007 Canonical sampling through velocity rescaling J. Chem. Phys. 126 014101

[34] Baroni S, De Gironcoli S, Corso A D and Giannozzi P 2001 Phonons and related crystal properties from density-functional perturbation theory Rev. Mod. Phys. 73 515

[35] Giannozzi P et al 2009 QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials J. Phys.: Condens. Matter 21 395502

[36] Shimanouchi T et al 1972 Tables of Molecular Vibrational Frequencies Consolidated Volume I (US Department of Commerce, National Bureau of Standards)

[37] Magnotti G, KC U, Varghese P L and Barlow R S 2015 Raman spectra of methane, ethylene, ethane, dimethyl ether, formaldehyde and propane for combustion applications J. Quant. Spectrosc. Radiat. Transfer 163 80–101

[38] Hirai H, Konagai K, Kawamura T, Yamamoto Y and Yagi T 2008 Phase changes of solid methane under high pressure up to 86 GPa at room temperature Chem. Phys. Lett. 454 212–17

[39] Pan D, Spanu L, Harrison B, Sverjensky D A and Galli G 2013 Dielectric properties of water under extreme conditions and transport of carbonates in the deep Earth Proc. Natl Acad. Sci. USA 110 6646–50

[40] Pan D, Wan Q and Galli G 2014 The refractive index and electronic gap of water and ice increase with increasing pressure Nat. Commun. 5 3919

[41] Zhang C, Donadio D, Gygi F and Galli G 2011 First principles simulations of the infrared spectrum of liquid water using hybrid density functionals J. Chem. Theory Comp. 7 1443–9

[42] Thalladi V R and Boese R 2000 Why is the melting point of propane the lowest among n-alkanes? New J. Chem. 24 579–81

[43] Nellis W J, Hamilton D C and Mitchell A C 2001 Electrical conductivities of methane, benzene and polybutene shock compressed to 60 GPa (600 kbar) J. Chem. Phys. 115 1015–19

[44] Bini R, Ulivi L, Jodl H J and Salvi P R 1995 High pressure crystal phases of solid CH$_4$ probed by Fourier transform infrared spectroscopy J. Chem. Phys. 103 1353–60

[45] Bini R and Pratesi G 1997 High-pressure infrared study of solid methane: phase diagram up to 30 GPa Phys. Rev. B 55 14800

[46] Buldakov M A, Korolev B V, Matrosov I I, Petrov D V and Tikhomirov A A 2013 Raman gas analyzer for determining the composition of natural gas J. Appl. Spectrosc. 80 124–8

[47] Gygi F, Fattebert J-L and Schwengler E 2003 Computation of maximally localized Wannier functions using a simultaneous diagonalization algorithm Comput. Phys. Commun. 155 1–6

[48] Marzari N, Mostofi A A, Yates J R, Souza I and Vanderbilt D 2012 Maximally localized Wannier functions: theory and applications Rev. Mod. Phys. 84 1419