Monolayer 2H-CrS$_2$ with intrinsic defect as a highly active catalyst for hydrogen evolution reaction

Aijun Hong$^{1*}$, Feng Sun$^1$, Wenda Zhou$^1$, Cailei Yuan$^{1*}$, Wei Zhang$^2$

*Correspondence and requests for materials should be addressed to A.J.H. (email: haj@jxnu.edu.cn) and C.L.Y. (email: clyuan@jxnu.edu.cn).

1 Jiangxi Key Laboratory of Nanomaterials and Sensors, School of Physics, Communication and Electronics, Jiangxi Normal University, Nanchang 330022, China
2 State Key Laboratory of Hydroscience and Engineering, Department of Energy and Power Engineering, Tsinghua University, Beijing 100084, China

**ABSTRACT:** Nanoscale transition-metal dichalcogenides (TMDs) have drawn ever-growing attention as a class of potential catalysts for hydrogen evolution reaction (HER). However, monolayer CrS$_2$ as one important number of nanoscale TMDs family receives few focuses, due to the difficulty of experimental synthesis. Recent work (Nanoscale, 2019, 11, 20123) reported monolayer CrS$_2$ with multiphase coexisting could be successfully prepared via the chemical vapor deposition (CVD). Thus, it is necessary to study on the stability and HER performance of 2H-CrS$_2$ structure as most likely to be synthesized first. In this work, by a combination of first-principles calculations and climbing image nudged elastic band method (ciNEB), we investigate mechanical, dynamical, and thermal stabilities and hydrogen evolution reaction (HER) performance of monolayer 2H-CrS$_2$. Our results suggest both S and Cr vacancies in the 2H-CrS$_2$ monolayer are excellent active sites. The free energies for the Volmer reaction in monolayers with Cr and S vacancies are respectively 0.11 eV and 0.07 eV, comparable with Pt-based catalyst. The defect states in the middle of bandgap and the enhanced interaction between the atomic layers result in high HER performance. We conclude that the monolayer 2H-CrS$_2$ with intrinsic S vacancy is a highly active catalyst and its HER is ascribe to the Volmer–Heyrovsky mechanism.
I. Introduction

In the past decades, layered two-dimensional (2D) materials, due to special physical and chemical properties, have received unprecedented attention [1-3]. Especially, nanoscale transition-metal dichalcogenides (TMDs) [4,5], as an important member of the 2D material family, present promising applications in energy field such as hydrogen evolution reaction (HER), battery and solar cell. Monolayer MoS$_2$/Si-based heterojunction has the highest power conversion efficiency of 5.23% [6] in all TMDs-based solar cells. Layered WS$_2$ nanosheets can effectively optimize the performance of Li–S battery due to polar adsorption. Because of high elemental abundance and high catalytic performance, MoS$_2$ has been regarded as a likely substitute of costly Pt-based catalyst for HER. For instance, the doped MoS$_2$ in the 2H structure has low onset potential of \(~0.13\) V and slight Tafel slope of 49 mV dec$^{-1}$ [7], exhibiting excellent catalytic performance. Moreover, Tafel slopes of WSe$_2$ and MoSe$_2$ nanofilms are 77.4 and 59.8 mV dec$^{-1}$, respectively [8]. However, there is little attention on chromium disulfide (CrS$_2$) because its bulk has not been experimentally synthesized. The monolayer CrS$_2$ cannot be obtained by mechanical exfoliation. Thankfully, recent work [9] claimed that monolayer CrS$_2$ with multiphase coexisting could be successfully prepared via the chemical vapor deposition (CVD). Considering that monolayer 2H-CrS$_2$ phase will most likely be synthesized first, it is necessary and interesting to explore its stability and HER performance. Meanwhile we find present theoretical method for assessing HER activity is rough, where only zero point energy (ZPE) are considered and are even ignored. It is also necessary to improve present assessing HER activity method.

Hence, in this work we employ density functional theory (DFT) to explore mechanical, dynamical, and thermal stabilities of 2H-CrS$_2$ monolayer. We put forward the improvement of assessing HER activity method and employ it to evaluate the HER activity of 2H-CrS$_2$ monolayer respectively with S vacancy (Vs) and with Cr vacancy (V$_{Cr}$) and the perfect monolayer (P). Our results show both Cr and S vacancies in the imperfect monolayer are excellent active sites. Their reaction free energies for the Volmer reaction are 0.11 eV and -0.07 eV, comparable with Pt-based catalyst. Using the
climbing image nudged elastic band method (ciNEB), we explore reaction pathways for Heyrovsky and Tafel reactions, and conclude the HER of the 2H-CrS$_2$ monolayer with intrinsic S vacancy belongs to the Volmer–Heyrovsky mechanism.

II. Calculation details and models

We add vacuum of 15 Å thick to all computational structures (4×4×1 supercells) for shielding the interaction between the periodic images, and geometrically optimize the structures by using VASP code [10-12]. In all DFT calculations, we adopt the generalized gradient approximation (GGA) and Perdew–Burke–Ernzerhof functional (PBE) [10,12] as the exchange correlation potential with a cutoff energy of 500 eV. For the calculations of structural optimization, the total energy and force criteria are set to less than $1 \times 10^{-4}$ eV and 0.03eV/Å, and a $k$-mesh of 5×5×1 is used. However, we increase $k$-mesh density to 11×11×1 for the calculation of electronic densities of states (DOS). The climbing image nudged elastic band (ciNEB) method [13] is employed to investigate HER mechanism. In this process, the force criteria are set to 0.04 eV/Å, and nine images are inserted between the initial and final states (IS and FS) to locate the reaction pathways and the transition states. Phonon structures are obtained by using Phonopy code [14], where the density functional perturbation method (DFPT) [15] and a 5×5×1 supercell are employed. Ab initio molecular dynamics (MD) simulation based on the canonical ensemble (NVT) [16,17] is employ to verify structural dynamical stability.

III. Results and discussion

A Stabilities of 2H-CrS$_2$ monolayer

| TABLE I. Calculated elastic constants of 2H-CrS$_2$ monolayer (units: GPa) |
|---------------------|---------------------|---------------------|---------------------|---------------------|
| $C_{11}$            | $C_{12}$            | $C_{13}$            | $C_{33}$            | $C_{44}$            |
| 64                  | 16                  | -21                 | -6                  | 2                   |
In this work, we use elastic constants, phonon spectrum, and ab initio molecular dynamics (MD) simulation to confirm mechanical, dynamical, and thermal stabilities. 2H-CrS₂ monolayer structure with the vacuum can be seen as three dimensional (3D) periodic image, belonging to the hexagonal crystal. Therefore, there are six independent elastic constants $C_{11}$, $C_{12}$, $C_{13}$, $C_{14}$, $C_{33}$ and $C_{44}$, as summarized in Table I. The elastic constants fulfill mechanical stability criteria [18], i.e., $C_{44} > 0$, $C_{66} > 0$, $C_{11} > |C_{12}|$, and $(C_{11} + 2C_{12})C_{33} > C_{13}^2$.

**TABLE II.** Calculated frequencies (units: cm$^{-1}$) of optical phonon modes at $\Gamma$ point for 2H-CrS₂ and 2H-MoS₂ monolayers.

|              | $A_2'$ | $A_1'$ | $E$  | $E'$ |
|--------------|--------|--------|------|------|
| 2H-CrS₂      | 507.6  | 397.1  | 416.7| 263.5|
| 2H-MoS₂      | 490.5  | 423.9  | 402.7| 298.2|

Admittedly, the elastic property of 2H-CrS₂ monolayer can also be described by the 3×3 elastic stiffness matrix [19]:

$$
\begin{pmatrix}
C_{11} & C_{12} & 0 \\
C_{12} & C_{22} & 0 \\
0 & 0 & C_{66}
\end{pmatrix},
$$

(1)

herein, $C_{66}$ is equal to $(C_{11}-C_{12})/2$. According to the Born criteria [20]: $C_{11} > 0$ and $C_{11}-C_{12} > 0$, which also ensures the 2H-CrS₂ monolayer is mechanically stable.

In Fig. 1, we present the phonon dispersion and phonon densities of states (PDOS) calculated within DFPT. The primitive cell of the 2H-CrS₂ monolayer has nine phonon modes, and belongs to the identical point group $D_{3h}$ like 2H-MoS₂ monolayer [21]. Thus, the irreducible representation for phonon at the Brillouin zone center point $\Gamma$ is as following [20]:

$$
\Gamma = 2A_2' \otimes A_1' \otimes 2E' \otimes E' \quad (2)
$$

where one $A_2'$ and one $E'$ are acoustic modes, the other $A_1'$ is infrared (IR) active, the other $E'$ is both Raman and IR active, the rest are IR active. The calculated frequencies of 2H-CrS₂ monolayer are illustrated in Table II, in comparison with the data [22] of
2H-MoS$_2$ monolayer. It is obvious their frequency differences are slight, due to the same structures and one identical element. Fig. 2b shows that PDOS in low frequency and high frequency ranges come from the joint contribution of Cr and S elements, although S element has a main contribution to the middle frequency range. It is obvious that there are no imaginary frequencies, fully verifying its dynamical stability.

Subsequently, to determine thermal stability, we carry out ab-initio molecular dynamics (MD) simulations of 2H-CrS$_2$ monolayer at 300 and 600 K, as shown in Fig. 2. We find the total energy remains small fluctuation and the structure has no obvious change, although the positions of atoms have slight movements. Therefore, 2H-CrS$_2$ monolayer is thermally stable in a wide temperature range from room temperature to medium temperature [23].

![Figure 1](image1.png)

**FIG. 1.** (a) Calculated phonon dispersion and (b) phonon densities of states.

![Figure 2](image2.png)

**FIG. 2.** Free energy as a function of time (a) at 300 K and (b) at 600 K.

**B Electronic structures**
FIG. 3. Calculated electronic band structures and DOS for P [(a) and (e)], V<sub>Cr</sub> [(b) and (f)] and V<sub>S</sub> [(c) and (g)].

Fig. 3 shows calculated electronic band structures and densities of states (DOS) of P, V<sub>Cr</sub> and V<sub>S</sub> systems. The perfect 2H-CrS<sub>2</sub> monolayer is a semiconductor with a direct bandgap of 0.99 eV that is in agreement with other calculated PBE bandgap of 1.07 eV [24]. The introduction of Cr or S vacancy induces defective states in the middle of bandgap. The defective states consists of strong hybridization of Cr and S atoms, indicating the vacancy can strength the coupling of atoms around the vacancy. On one hand, the defective states lying around the Fermi level promote the electrical conductivity via providing enough carriers, which can bring about significant electrocatalytic performance [25,26]. On the other hand, the vacancy changes the total potentials (see Fig. 4). All the total potential curves like double-hump shape, corresponding to the sandwich structure of 2H-CrS<sub>2</sub> monolayer. Two S atomic layers have relatively low total potentials and Cr atomic layer’s is high. Thus, to participate in
the HER, an electron in the S atomic layer needs to overcome the potential wells to the other sulfur layer, and then crosses the last potential well to reach the surface. The depth of the last potential well in Vs system is 2 eV smaller than that for P and VCr systems, which supports high electron tunneling probability and thus improves HER performance.

![Total potential distribution along the c axis.](image)

**FIG. 4.** Total potential distribution along the c axis.

**C HER performance and mechanism**

The HER, as a tanglesome electrochemical process, usually happens on the surface of catalyst. At present, there are two recognized mechanisms for HER in acid solution [27]: one is Volmer-Heyrovsky reaction and the other is Volmer-Tafel reaction. The former reaction process includes two steps. First electrochemical hydrogen adsorption, namely, Volmer reaction takes place,

\[
\text{H}^+ + e^- + X = \text{H}^*-X ,
\]

and then electrochemical desorption (Heyrovsky reaction) occurs, as follows:

\[
\text{H}^*-X + e^- + \text{H}^+ = X + \text{H}_2 .
\]

However, Volmer-Tafel reaction possesses the different way of H desorption (Tafel reaction),

\[
\text{H}^*-X-\text{H}^* = X + \text{H}_2 ,
\]

herein, H* is a hydrogen atom adsorbed on the active site of catalyst surface. In a word, the difference between the two mechanisms lies in the different ways of H desorption.
Adsorption and desorption of H atom on the catalyst surface have competitive relation. Thus, the balance between adsorption and desorption is important for a high-efficiency catalyst. According to the Sabatier’s principle [28], to achieve the balance, the free energy differences ($\Delta G = G_P - G_R$) between the free energies of product and reactant ($G_P$ and $G_R$) in each reaction, namely, the reaction free energies should be near zero. We define the free energy of product and reactant ($G_P$ and $G_R$) as the following form

$$G = E_{ele} + E_{vib} - TS_{vib}$$

where $E_{ele}$ is the total energy associated with electrons, $E_{vib}$ the vibrational energy, $T$ absolute temperature, $S$ the vibrational entropy. Both the vibrational energy and entropy of an $N$-atomic system can be attained by the partition function:

$$Z = \sum_{l=1}^{N} \sum_{n=0}^{\infty} e^{-\beta \omega_n l}$$

(7)

where $\beta = 1/kT$ ($k$: Boltzmann constant) and the $\omega_n$ has $3N$ vibrational modes. Then, the vibrational energy and entropy are given by

$$E_{vib} = -\frac{\partial}{\partial \beta} \ln Z$$

(8)

and

$$S_{vib} = k(\ln Z + \beta E_{vib})$$

(9)

Using Eq. (7) in Eqs. (8) and (9), one can finally write

$$E_{vib} = \sum_{i=1}^{N} h \omega_i \left(\frac{1}{2} + \frac{1}{e^{\beta \omega_i} - 1}\right)$$

(10)

and

$$S_{vib} = \sum_{i=1}^{N} k \left[\frac{\beta h \omega_i}{e^{\beta \omega_i} - 1} - \ln(1 - e^{-\beta \omega_i})\right].$$

(11)

When the temperature approaches to 0 K, the vibrational energy is written as

$$E_{vib} = \sum_{i=1}^{N} \frac{1}{2} h \omega_i ,$$

(12)

which are also called zero point energy ($E_{ZPE}$). Table II illustrates $E_{vib}$ and $TS_{vib}$ of one adsorbed H on the surfaces of P$_{Cr}$, P$_{S}$, V$_{Cr}$ and V$_{S}$ systems. These values for all systems except P$_{Cr}$ are comparable with $E_{vib}$ (0.14 eV ) and $TS_{vib}$ (0.2 eV) for one H atom of the H$_2$ gas molecule under standard conditions, indicating that $E_{vib}$ and $TS_{vib}$ can not be ignored.
TABLE III. Calculated vibrational energy $E_{vib}$ and entropy $S_{vib}$ at 298 K and $E_{ZPE}$ for P$_{Cr}$, P$_{S}$, V$_{Cr}$ and V$_{S}$. Experimental vibrational energy $E_{vib}$ and standard entropy $S_{vib}$ for H$_2$ gap molecule (units: eV).

|          | P$_{Cr}$ | P$_{S}$ | V$_{Cr}$ | V$_{S}$ | H$_2$ |
|----------|----------|----------|----------|----------|-------|
| $E_{vib}$ (T=298K) | 0.0990   | 0.2367   | 0.2240   | 0.1587   | 0.28 [29] |
| $TS_{vib}$ (T=298K) | 0.0001   | 0.0105   | 0.0117   | 0.0090   | 0.40 [26] |
| $E_{ZEP}$ | 0.0987   | 0.2287   | 0.2153   | 0.1517   | -     |

Finally, the reaction free energies of Volmer ($\Delta G_{in}^\psi$), Heyrovsky ($\Delta G^n$) and Tafel ($\Delta G^\psi$) reactions can be computed using the following formulas

$$\Delta G_{in}^\psi = \Delta E_{in} + \Delta E_{vib} - T \Delta S,$$

(13)

$$\Delta G^n = -\Delta G_{in}^\psi,$$

(14)

$$\Delta G^\psi = -\Delta G_{in}^\psi - \Delta G_{in+1}^\psi.$$

(15)

As known, the Volmer reaction is the preliminary and foremost step in the HER. Therefore, we first put focus on the Volmer reaction taking place on the surfaces of different systems. All the possible H-adsorption sites in each surface have been taken account, and the typical adsorption configurations with the lowest total energy are displayed in Figure 2a, where the perfect monolayer, the imperfect monolayer with Cr vacancy and with S vacancy are respectively marked with P, V$_{Cr}$ and V$_{S}$. P$_{Cr}$ and P$_{S}$ stand for the P system with H-adsorption on the top of Cr and with H-adsorption on the top of S, respectively. The bond length of S-H in P$_{S}$ is 1.36 Å that is shorter than the Cr-H bond length of 1.64 Å in P$_{Cr}$, suggesting the S site is possibly higher catalytically active. This is further confirmed by the reaction energies of P$_{Cr}$ and P$_{S}$. The $\Delta G_{in}^\psi$ for P$_{S}$ is 1.35 eV that is smaller than 1.76 eV for P$_{Cr}$. For V$_{Cr}$ structure, H atom chemically binds to a prominent S atom with the S-H bond length of 1.37 Å, and the Cr-H distance is about 3 Å, implying weak interaction between Cr and H atoms. For V$_{S}$ structure, the distance between H atom and the three nearest neighbor Cr atoms is 1.92 Å, and that between H atom and the nearest neighbor S atom is 2.4 Å implying relatively weak H-
S bond. The $\Delta G_{\text{f}}^*$ for both $V_S$ and $V_{Cr}$ are very close to 0 eV, comparable with Pt-based catalyst. This fully illustrates that the Cr and S vacancies as two types of intrinsic defects are efficient active sites in the imperfect 2H-CrS$_2$ monolayer.

![Optimized atomic configurations and reaction energies](image.png)

**FIG. 5.** Upper panel: optimized atomic configurations in turn for $P_{Cr}$, $P_{S}$, $V_{Cr}$ and $V_{S}$. Lower panel: their reaction energies for the Volmer reaction.

The formation energy of Cr vacancy is much larger than that for S vacancy, leading to the scarcity of Cr vacancy in the monolayer. This determines that the $V_{Cr}$ structure cannot be an efficient hydrogen evolution material. Thus, we emphatically discuss the mechanism of HER for only $V_{S}$ structure. $\Delta G_{H}$ for the Volmer, Heyrovsky, and Tafel reactions are presented in Fig. 6(a). Both first and second Volmer reactions are exothermic due to $\Delta G_{H} = 0.07$ eV and 0.41 eV. $\Delta G_{H}$ for the Heyrovsky reaction is closer to zero than that for the Tafel reaction. From the perspective of reaction free energy, the Volmer-Heyrovsky reaction seems prone to occur, but such judgment is crude and unreliable, due to the existing of the reaction barrier.

Thus, it is necessary to explore the reaction pathways for HER in order to determine the reaction mechanism. Figs. 6(a) and 6(b) respectively show the reaction pathways of the Heyrovsky and Tafel reactions on the surface of the $V_{S}$ system. For the Tafel reaction, the release of a hydrogen gas molecule through the recombination of $2H^+$ needs to cross a transition state with a big energy barrier (0.64 eV), whereas a free
proton and an adsorbed H forming a hydrogen gas in the Tafel reaction has nearly no energy barrier. This obviously indicates that the HER on the surface of the 2H-CrS\textsubscript{2} with S vacancy is prone to the Volmer-Heyrovsky mechanism.

**FIG. 6.** (a) Sketch of Volmer, Heyrovsky and Tafel reactions on the surface of Vs, reaction pathways of (b) the Heyrovsky reaction and the Tafel reaction.

**IV. CONCLUSION**

In this work, mechanical, dynamical, and thermal stabilities of 2H-CrS\textsubscript{2} monolayer are confirmed, and the electronic structures and HER performance and mechanism for the perfect and imperfect 2H-CrS\textsubscript{2} monolayers are explored. It is found that the introductions of Cr or S vacancy can induces defect states into the middle of bandgap. We consider the defect states composed of the hybridization of Cr and S can increase electrical conductivity and thus enhance HER performance. Furthermore, we put forward a new effective strategy to evaluate the HER activity. The vibrational energy and entropy instead of the zero point energy (ZPE) is taken into account in the strategy, which more approaches to the practical HER. Using the strategy, our results indicate there are no efficient active sites in the perfect 2H-CrS\textsubscript{2} monolayer. However, both Cr and S vacancies in the imperfect monolayer are excellent active sites. We predicted the
2H-CrS₂ monolayer with intrinsic defect S vacancy can be considered as the highly active HER catalyst and its HER is prone to the Volmer–Heyrovsky mechanism.

**Acknowledgment:**

This work is supported by the National Natural Science Foundation of China (Grant No. 11804132).

**References**

[1] K. S. Novoselov, Reviews of Modern Physics 83, 837 (2011).
[2] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, Nature Nanotechnology 7, 699 (2012).
[3] J. Z. Jiang, C. P. Y. Wong, J. Zou, S. S. Li, Q. X. Wang, J. Y. Chen, D. Y. Qi, H. Y. Wang, G. Eda, D. H. C. Chua, Y. M. Shi, W. J. Zhang, and A. T. S. Wee, 2d Materials 4, 021026 (2017).
[4] A. J. Hong, Applied Surface Science 473, 6 (2019).
[5] Y. Z. Meng, C. Y. Ling, R. Xin, P. Wang, Y. Song, H. J. Bu, S. Gao, X. F. Wang, F. Q. Song, J. L. Wang, X. R. Wang, B. G. Wang, and G. H. Wang, Npj Quantum Materials 2, 16 (2017).
[6] M. L. Tsai, S. H. Su, J. K. Chang, D. S. Tsai, C. H. Chen, C. I. Wu, L. J. Li, L. J. Chen, and J. H. He, Acs Nano 8, 8317 (2014).
[7] X. L. Huang, M. Leng, W. Xiao, M. Li, J. Ding, T. L. Tan, W. S. V. Lee, and J. M. Xue, Advanced Functional Materials 27, 1604943 (2017).
[8] H. T. Wang, D. S. Kong, P. Johannes, J. J. Cha, G. Y. Zheng, K. Yan, N. A. Liu, and Y. Cui, Nano Letters 13, 3426 (2013).
[9] M. R. Habib, S. P. Wang, W. J. Wang, H. Xiao, S. M. Obaidulla, A. Gayen, Y. Khan, H. Z. Chen, and M. S. Xu, Nanoscale 11, 20123 (2019).
[10] P. E. Blöchl, Physical Review B 50, 17953 (1994).
[11] G. Kresse and J. Furthmüller, Physical Review B 54, 11169 (1996).
[12] J. P. Perdew, K. Burke, and M. Ernzerhof, Physical Review Letters 77, 3865 (1996).
[13] G. Henkelman, B. P. Uberuaga, and H. Jónsson, The Journal of Chemical Physics 113, 9901 (2000).
[14] A. Togo, F. Oba, and I. Tanaka, Physical Review B 78, 134106 (2008).
[15] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Reviews of Modern Physics 73, 515 (2001).
[16] W. G. Hoover, Physical Review A 31, 1695 (1985).
[17] L. Verlet, Physical Review 159, 98 (1967).
[18] F. Mouhat and F. X. Coudert, Physical Review B 90, 224104 (2014).
[19] D. Liu, A. G. Every, and D. Tomanek, Physical Review B 94, 165432 (2016).
[20] Y. Qi and L. G. Hector, Applied Physics Letters 90, 081922 (2007).
[21] S. Y. Chen, C. X. Zheng, M. S. Fuhrer, and J. Yan, Nano Letters 15, 2526 (2015).
[22] Y. Q. Cai, J. H. Lan, G. Zhang, and Y. W. Zhang, Physical Review B 89, 035438 (2014).
[23] F. Q. Wang, S. H. Zhang, J. B. Yu, and Q. Wang, Nanoscale 7, 15962 (2015).
[24] C. Ataca, H. Sahin, and S. Ciraci, Journal of Physical Chemistry C 116, 8983 (2012).
[25] H. B. Shu, D. Zhou, F. Li, D. Cao, and X. S. Chen, Acs Applied Materials & Interfaces 9, 42688 (2017).
[26] Y. Y. Zhang, H. W. Lei, D. L. Duan, E. Villota, C. Liu, and R. Ruan, Acs Applied Materials & Interfaces 10, 20429 (2018).
[27] J. K. Norskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov, and J. K. Norskov, Journal of the Electrochemical Society 152, J23 (2005).
[28] Y. X. Ouyang, C. Y. Ling, Q. Chen, Z. L. Wang, L. Shi, and J. L. Wang, Chemistry of Materials 28, 4390 (2016).
[29] N. Jonathan, C. M. Melliar-Smith, S. Okuda, D. H. Slater, and D. Timlin, Molecular Physics 22, 561 (1971).