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Theoretical calculation of hydrogen molecule in silicon

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First principle quantum chemical calculations have been performed on a hydrogen molecule in the silicon crystal using the cluster model of $\text{Si}_{10}\text{H}_{16}$. The *ab initio* molecular orbital theory and the density functional theory (DFT) calculations have been examined. In all calculations, the tetrahedral site is the most stable trapping site for the hydrogen molecule. The DFT calculations with generalized gradient approximation show that the bond length of H_2 in the silicon crystal is comparable to that of gaseous H_2 . The calculated vibrational frequency of H_2 in the silicon crystal agrees well with the experimental value obtained by Murakami *et al.* [Phys. Rev. Lett. **77**, 3161 (1996)]. © 1998 American Institute of Physics. [S0021-9606(98)01008-3]

I. INTRODUCTION

Hydrogen is the simplest impurity and plays an important role in improving the electrical properties of semiconductors such as termination of dangling bonds and passivation of deep level impurities.¹ The states of hydrogen in silicon crystals have been investigated extensively, and various configurations of hydrogen atoms bound to lattice atoms and/or impurities have been reported such as donor/acceptor-H complexes,^{1,2} and {111} platelets.³ Recently Murakami and co-workers⁴⁻⁶ have studied a silicon wafer exposed to hydrogen atoms at around 400 °C using Raman spectroscopy and found that hydrogen molecules are formed in crystalline silicon. They have observed a vibrational line (Q_1) of H_2 at $4158 \pm 3 \text{ cm}^{-1}$ and a rotational H_2 line [$S_0(1)$] at 590 cm^{-1} , whose Raman shifts are comparable to those of gaseous H_2 . The Q_1 and $S_0(1)$ denote the transitions of ($\Delta\nu=1$ and $\Delta J=0$) and ($\Delta\nu=0$, $\Delta J=2$, and $J=1$), where ν and J are the vibrational and rotational quantum numbers, respectively. Anharmonic effects are important in H_2 and the Q_1 frequency includes both harmonic and anharmonic terms. The harmonic frequency of H_2 in Si was estimated to be about 4400 cm^{-1} using an anharmonic value of 121 cm^{-1} .

Theoretical calculations have been performed on the status of hydrogen in silicon with various techniques and suggested that hydrogen molecule is stable in silicon crystal.^{1,7-16} Chadi *et al.*¹⁴⁻¹⁶ calculated the total energies and the defect level of various hydrogen-related defects using the *ab initio* pseudopotential method, and showed that the hydrogen molecule is stable at the tetrahedral (T_d) interstitial site in silicon crystal with its molecular axis along the $\langle 111 \rangle$ or the $\langle 100 \rangle$ direction. The bond length of the hydrogen molecule at the T_d site is calculated to be 0.78 \AA , about 0.04 \AA longer than in the gas phase. Van de Walle *et al.*^{7,8} calculated the total energy of the hydrogen molecule in silicon and its frequency using the density function theory (DFT) in local density approximation (LDA) with *ab initio* pseudopotentials and plane-wave functions. He found that a hydrogen

molecule is stable at the T_d site with its bond length of 0.86 \AA and that its vibrational frequency is an unreasonably small value (2300 cm^{-1}). Although the vibrational frequency is a fingerprint used for a benchmark for theoretical calculations, systematic calculations on the vibrational frequency of the hydrogen molecule in the silicon crystal has not been performed until now.

In previous papers^{17,18} we have performed *ab initio* Hartree-Fock (HF) calculations of H_2 in silicon using the $\text{Si}_{10}\text{H}_{16}$ cluster and the small Gaussian-type basis set (3-21 G). The results showed that H_2 is also stable at the T_d site of the $\text{Si}_{10}\text{H}_{16}$ cluster. The calculated frequency (4849 cm^{-1}) was much closer to the experimental estimate than that of the calculation by van de Walle, but slightly ($\sim 200 \text{ cm}^{-1}$) higher than that of a free H_2 obtained with the same level calculation. In the calculations we neglected a relaxation of the cluster and the electron correlation interaction effect. In the present paper, we performed *ab initio* molecular orbital calculations and the first-principle DFT calculations with taking into account the cluster-relaxation, higher basis sets, and the correlation interaction. The stability and the diffusion of H_2 in Si will be also discussed.

II. COMPUTATIONAL DETAILS

The silicon lattice was modeled with the cluster ($\text{Si}_{10}\text{H}_{16}$) of 10 Si atoms, where H atoms were put in order to hold sp^3 configurations of the Si bonds. Figure 1 shows the 10 Si atoms of the cluster and a unit cell of a silicon crystal. Two H atoms were set in the cluster. A full geometry optimization was performed for the system of H_2 in the $\text{Si}_{10}\text{H}_{16}$ cluster without assuming constraint in symmetry and geometry using initial parameters of the Si-Si bond length of the Si crystal (2.352 \AA), the Si-H bond length of the silane molecule (1.480 \AA),¹⁹ and the sp^3 configuration. All the calculations were performed with GAUSSIAN 94 programs²⁰ on the workstations (IBM RS/6000 SP and SGI Indigo 2 Extreme R10000). *Ab initio* molecular orbital calculations were

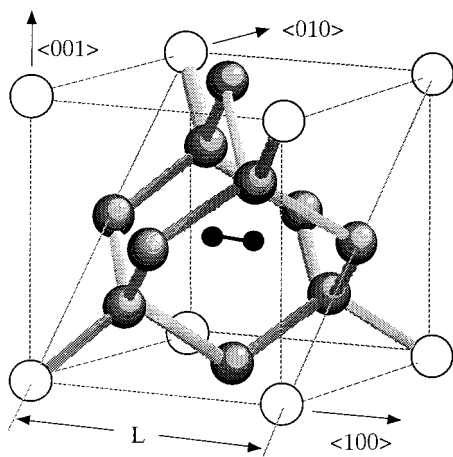


FIG. 1. A schematic drawing of the unit cell of the silicon crystal and the cluster with 10 silicon atoms. White circles, shaded circles, and black circles are Si atoms of the unit cell, Si atoms in the cluster, and hydrogen atoms, respectively. The cluster size (L) corresponds to the lattice constant of the silicon crystal.

performed with the restricted-HF (RHF) theory and Møller–Plesset perturbation theory (MP2). The DFT calculations were performed with a local spin density approximation (LSDA) and a generalized gradient approximation (GGA). In the LSDA, the Slater exchange functional, and the Vosko–Wilk–Nusair (VWN) (Ref 21) correlational functional were used. In the GGA, BPW91, BLYP, and B3LYP methods were used. The BPW91 uses the Becke’s exchange functional,²² which includes the Slater exchange along with corrections involving the gradient of the density, and Perdew and Wang (PW) (Ref. 23) correlation functional. The BLYP uses the Becke’s exchange functional,²² and Lee–Yang–Parr (LYP) (Ref. 24) correlation functional, which includes both local and nonlocal terms. The B3LYP includes nonlocal electron correlation interactions and uses the exchange–correlation energy E_{xc} expressed by,

$$E_{xc} = E_{xc}^{\text{LSDA}} + A(E_x^{\text{exact}} - E_x^{\text{LSDA}}) + B\Delta E_x^{B88} + C\Delta E_c^{\text{LYP}},$$

where A , B , and C are semiempirical coefficients to be determined by appropriate fit to experimental data, E_x^{exact} is the exact exchange energy, ΔE_x^{B88} is Becke’s gradient correction²² to the LSDA exchange, ΔE_c^{LYP} is the LYP gradient correction for correlation, and E_{xc}^{LSDA} and E_x^{LSDA} are exchange–correlation and exchange energies of LSDA, respectively.²⁵ The geometry optimization was performed with each level of the method. Used basis sets were Gaussian-type functions, 3-21G and 6-31G* for RHF, 3-21G for MP2, 6-31G* for LSDA, BPW91 and BLYP, and 6-31G* and 6-31+G* for B3LYP.

III. RESULTS AND DISCUSSIONS

A. Bond length and vibrational frequency

In order to assess the accuracy of the present calculation, we first compute the equilibrium bond length and vibrational frequency of a free H_2 molecule (Table I). The calculated bond lengths are underestimated by -0.94% to -1.75% in RHF. In accord with the underestimated bond length, the

TABLE I. The bond length [$R(\text{HH})$, (Å)], the harmonic vibrational frequency [ω_0 , (cm^{-1})], and the energy (hartree) of a free hydrogen molecule.

Method	Basis set	$R(\text{HH})$	ω_0	Energy
Expt		0.742 ^a	4400 ^a	
RHF	3-21G	0.735	4654	-1.1229
RHF	6-31G*	0.729	4647	-1.1403
MP2	3-21G	0.741	4552	-1.1403
LSDA	6-31G*	0.763	4227	-1.1685
BPW91	6-31G*	0.748	4375	-1.1725
BLYP	6-31G*	0.748	4377	-1.1652
B3LYP	6-31G*	0.743	4454	-1.1755
B3LYP	6-31+G*	0.743	4453	-1.1755

^aReference 31.

calculated vibrational frequency differs from the experimental value by 5.77%–5.61%. It is known that HF calculations overestimate the vibrational frequency by about 10% due to the neglect of the correlation interaction. The calculated bond length in MP2, which includes the correlation interaction, agrees well with the experimental value but the vibrational frequency is overestimated by 3.45%. The DFT calculation includes the correlation interaction in principle. The calculated bond length in the LSDA is overestimated by 2.83% and the calculated vibrational frequency differs -3.93% from the experimental value. It is known that the bond length of a small molecule is overestimated in the local density approximation. The calculated bond lengths in BLYP and BPW91 are overestimated by 0.81% and the calculated vibrational frequencies differ -0.52% from the experimental value. In B3LYP calculations, which is the highest level calculation in the present study, the calculated bond length and vibrational frequency agree well with the experimental values. The results show that the nonlocal correlation interaction effect is important and that B3LYP would be the most suitable calculation method in the present study.

Next we search for stable sites for a H_2 molecule in a silicon crystal using the cluster model. All the calculations of the geometry optimization showed that the trapping site of H_2 with the minimum energy was the T_d site, and the H_2 molecular axis oriented in the $\langle 100 \rangle$ direction. Table II shows

TABLE II. The bond length [$R(\text{HH})$, (Å)], the harmonic vibrational frequency [ω_0 , (cm^{-1})], and the energy (hartree) of H_2 in the $\text{Si}_{10}\text{H}_{16}$ cluster. $\Delta\omega_0$ and ΔR are the differences in the vibrational frequency and the bond lengths between free H_2 and H_2 in the cluster calculated with each method, respectively. The cluster size [L , (Å)] corresponds to the lattice constant of the Si crystal includes H_2 (see Fig. 1).

Method	Basis set	$R(\text{HH})$	ΔR	ω_0	$\Delta\omega_0$	L	Total energy
Expt				-4400 ^a			
RHF	3-21G	0.708	-0.027	4849	195	5.57	-2884.2812
RHF	6-31G*	0.709	-0.014	4969	322	5.51	-2884.3939
MP2	3-21G	0.727	-0.014	4649	197	5.57	-2884.3939
LSDA	6-31G*	0.789	+0.026	3773	-454	5.45	-2897.0708
BPW91	6-31G*	0.764	+0.016	4020	-355	5.46	-2905.6232
BLYP	6-31G*	0.747	-0.001	4380	3	5.55	-2905.4424
B3LYP	6-31G*	0.739	-0.004	4468	14	5.47	-2905.7524
B3LYP	6-31+G*	0.740	-0.003	4470	17	5.54	-2905.7543

^aThe harmonic frequency was estimated from the observed Q_1 transition (4158 cm^{-1}) and an unharmonic term of 121 cm^{-1} (Ref. 6 and 31).

the results of the calculations. The calculated bond length of H_2 in the Si crystal in RHF and MP2 was shorter than that of free H_2 by -1.89 to -3.67% . In accord with the shorter bond length, the vibrational frequency was higher shifted by 2.13% – 6.93% . In the LSDA calculation, the calculated bond length was longer than that of free H_2 by 3.41% and the vibrational frequency was lower shifted by -10.74% . In the BPW91 calculation, the calculated bond length was longer than that of free H_2 by 2.16% and the vibrational frequency was lower shifted by -8.07% . The interaction between H atoms and surround Si atoms in LSDA and BPW91 is stronger than that in HF and MP2. The calculated bond length and vibrational frequency in BLYP and B3LYP are comparable to those of a free H_2 molecule. The difference in the bond length was -0.01% to -0.54% and that in the vibrational frequency 0.07% – 0.31% . There is no significant difference in calculations with the $6-31G^*$ and the diffused $6-31+G^*$ basis sets. The BLYP and B3LYP calculations agree well with the recent experimental results, which shows that the observed vibrational frequency of H_2 in the silicon crystal is comparable to that of a free H_2 molecule. It is reported that B3LYP calculations also reproduce well the vibrational frequencies of Si–H on the Si(100) surface using a cluster model.²⁶

Very recently Van de Walle recalculated the H_2 in the silicon crystal using the LDA *ab initio* pseudopotentials, and plane-wave basis sets with energy cutoff of 48 Ry.²⁷ Interstitial H_2 was calculated in 32-atoms supercells. He obtained that the H_2 molecule orients along the $\langle 100 \rangle$ direction at the T_d site. The calculated bond length was stretched (0.817 \AA) and the vibrational frequency was lower shifted (3396 cm^{-1}). Similar results were obtained in the present LSDA calculation. LDA gives the longer bond length and the lower vibrational frequency. In his calculation the bond length and vibrational frequency of the free H_2 molecule were calculated to be 0.771 \AA and 4135 cm^{-1} . The obtained values are very different from the experimental values, making his results unreliable. The similar results of free H_2 and H_2 in the silicon crystal were also reported by Okamoto *et al.*²⁸ using LDA and GGA with the plane-wave basis sets. It may not be adequate to calculate H_2 using the plane-wave basis sets.

B. Stability of H_2 in silicon crystal

We studied the stability of the H_2 molecule in the silicon crystal using B3LYP ($6-31+G^*$) calculations. The full structural optimization gave that the most stable state is H_2 oriented along the $\langle 100 \rangle$ direction at the T_d site. In this computational level, the cluster size (L) of the cluster including H_2 was obtained to be 5.54 \AA , which is 1.6% longer than that of the cluster without including H_2 (5.45 \AA).²⁹ Figure 2 shows the total charge density calculated with B3LYP ($6-31+G^*$) in the (001) plane. The charge density of H_2 is almost isolated from the surround Si and weakly interacts with two Si atoms in the direction of the molecular axis. The rotational barrier of H_2 at the T_d site was calculated to be very small ($<30 \text{ meV}$). For example, the energy of H_2 oriented along

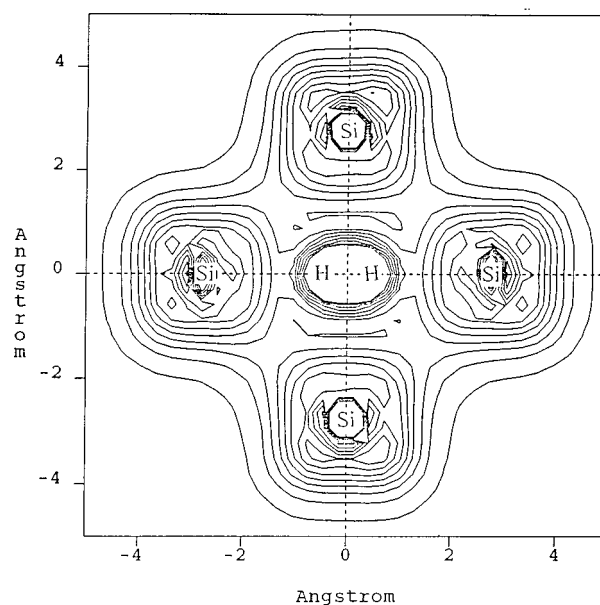


FIG. 2. The contour plot of the charge density for H_2 in the $Si_{10}H_{16}$ cluster in the (001) plane calculated with the B3LYP ($6-31+G^*$). Contours are shown in the range between 0 and 0.5 in the atomic unit with a spacing of 0.05.

the $\langle 111 \rangle$ direction was 18 meV higher than that along the $\langle 100 \rangle$. Therefore H_2 can rotate at the T_d site at room temperature (25 meV).

The energy of H_2 in the silicon cluster has a local minimum at the hexagonal (H_{ex}) site during the geometry optimization. However the system of H_2 at the H_{ex} site has one imaginary frequency which corresponds to the translational mode of H_2 in the cluster. The H_{ex} site is considered to be a transition state of the diffusion of H_2 through a T_d – H_{ex} – T_d path. The energy of H_2 at the H_{ex} site was 1.22 eV higher than that of H_2 at the T_d site. Therefore the diffusion barrier of H_2 in the silicon crystal is estimated to be 1.22 eV . The barrier is high enough to trap H_2 in the silicon crystal at room temperature. Recently Fukata *et al.*³⁰ have performed annealing experiments for H_2 in the silicon crystal at temperatures between 250 – $600 \text{ }^\circ\text{C}$ and estimated the diffusion barrier to be about 1.6 eV . The diffusion barrier calculated in the present study is in reasonable agreement with the experimental estimate.

Figure 3 shows the energy diagram for various forms of the $H_2/Si_{10}H_{16}$ system. The zero energy was set to be the energy of H_2 at the T_d site. The state of H_2 at the H_{ex} site is the transition state for going out of the cluster. The lowest energy state was the state that the H_2 molecule exits outside the cluster ($H_2 + Si_{10}H_{16}$) and its energy was 1.6 eV lower than that of H_2 at the T_d site. If the H_2 molecule dissociate to two H atoms outside the cluster, the energy of the system ($2H + Si_{10}H_{16}$) was 2.9 eV higher than that of H_2 at the T_d site. Therefore the hydrogen atoms can enter the silicon crystal and form the H_2 molecule but the gas phase H_2 molecule cannot enter the silicon crystal, which is consistent with the experiment in which the H_2 is formed by the hydrogen atom treatment on a Si wafer.^{6,30}

In summary, first principle theoretical calculations of hy-

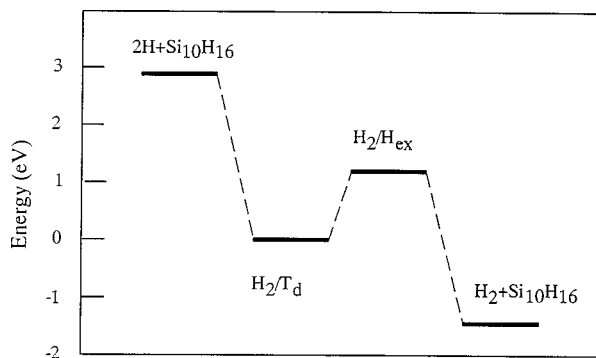


FIG. 3. The energy diagram of H_2 and the $Si_{10}H_{16}$ cluster. $2H+Si_{10}H_{16}$, $H_2+Si_{10}H_{16}$, H_2/T_d , and H_2/H_{ex} denote two H atoms outside the cluster, H_2 molecule outside the cluster, H_2 molecule at the T_d site, and H_2 molecule at the H_{ex} site, respectively.

drogen molecules in the $Si_{10}H_{16}$ cluster were performed with the *ab initio* HF and the DFT methods. The calculations showed that the T_d site is the stable trapping site for the hydrogen molecule. B3LYP calculations showed that the bond length and the vibrational frequency of H_2 in the silicon crystal are comparable to those of the free H_2 , which reproduces well the recent Raman experiment. The diffusion barrier of H_2 in the silicon crystal was estimated to be 1.22 eV.

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¹*Hydrogen in Crystalline Semiconductors*, edited by S. J. Pearton, J. W. Corbett, and M. Stavola (Springer, New York, 1992).

²K. Bergman, M. Stavola, S. J. Pearton, and J. Lopata, *Phys. Rev. B* **37**, 2770 (1988).

³N. M. Johnson, F. A. Ponce, R. A. Street, and R. J. Nemanich, *Phys. Rev. B* **35**, 4166 (1987).

⁴N. Fukata, S. Sasaki, K. Murakami, K. Ishioka, M. Kitajima, S. Fujimura, and J. Kikuchi, *Jpn. J. Appl. Phys., Part 1* **35**, L1069 (1996).

⁵K. Murakami, N. Fukata, S. Sasaki, K. Ishioka, M. Kitajima, S. Fujimura, J. Kikuchi, and H. Haneda, *Phys. Rev. Lett.* **77**, 3161 (1996).

⁶N. Fukata, S. Sasaki, K. Murakami, K. Ishioka, K. G. Nakamura, M. Kitajima, S. Fujimura, J. Kikuchi, and H. Haneda, *Phys. Rev. B* **56**, 6642 (1997).

⁷C. G. Van de Walle, P. J. H. Denteneer, Y. Bar-Yam, and S. T. Pantelides, *Phys. Rev. B* **39**, 10791 (1989).

⁸C. G. Van de Walle, *Phys. Rev. B* **49**, 4579 (1994).

⁹P. Deak, L. C. Snyder, R. K. Singh, and J. W. Corbett, *Phys. Rev. B* **36**, 9612 (1987).

¹⁰P. Deak, and L. C. Snyder, *Phys. Rev. B* **36**, 9619 (1987).

¹¹P. Deak, L. C. Snyder, J. L. Lindstrom, J. W. Corbett, S. J. Pearton, and A. J. Tavendale, *Phys. Lett. A* **126**, 427 (1988).

¹²S. K. Estreicher, *Phys. Rev. B* **36**, 9122 (1987).

¹³S. K. Estreicher, M. A. Roberson, and Dj. M. Maric, *Phys. Rev. B* **50**, 19018 (1994).

¹⁴K. J. Chang and D. J. Chadi, *Phys. Rev. Lett.* **60**, 1422 (1988).

¹⁵K. J. Chang and D. J. Chadi, *Phys. Rev. Lett.* **62**, 937 (1989).

¹⁶D. J. Chadi and C. H. Park, *Phys. Rev. B* **52**, 8877 (1995).

¹⁷K. G. Nakamura, K. Ishioka, M. Kitajima, and K. Murakami, *Solid State Commun.* **101**, 753 (1997).

¹⁸K. G. Nakamura and M. Kitajima, *Jpn. J. Appl. Phys., Part 1* **36**, 2004 (1997).

¹⁹*CRC Handbook of Chemistry and Physics*, edited by D. R. Lide and H. P. R. Frederikse (Chemical Rubber, Boca Raton, 1995).

²⁰GAUSSIAN 94, Revision C.3, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wang, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, Pennsylvania, 1995.

²¹S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).

²²A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).

²³J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).

²⁴C. Lee, and W. Yang and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).

²⁵A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).

²⁶M. K. Weldon, B. B. Stefanov, K. Raghavachari, and Y. J. Chabal, *Phys. Rev. Lett.* **79**, 2851 (1997).

²⁷C. G. Van de Walle, *Phys. Rev. Lett.* (to be published).

²⁸Y. Okamoto, M. Saito, and A. Oshiyama, *Phys. Rev. B* **56**, 10016 (1997).

²⁹The calculated lattice constant from the cluster without including H_2 (5.45 Å) agrees well with the experimental value (5.43 Å) of the silicon crystal.

³⁰N. Fukata, K. Murakami, K. Ishioka, K. G. Nakamura, M. Kitajima, and J. Fujimura, *Phys. Rev. B* (submitted).

³¹K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979), p. 250.