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van der Waals interactions between molecular hydrogen and alkali-metal atoms

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In this paper, we have calculated the values of the C_6 coefficients and the anisotropy parameters γ of the leading term of the van der Waals interactions between molecular hydrogen and alkali-metal atoms from Li to Fr. The uncertainties in our results are less than 2%.

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I. INTRODUCTION

Collisions at ultralow temperatures are sensitive to long-range interactions between the colliding species. Of particular importance in the construction of the long-range potential are the C_6 coefficient and the anisotropy parameter γ of the leading term of the van der Waals interaction, which decreases with nuclear separation R as R^{-6} . These two constants can be obtained by integration over the frequency ω of the product of the dynamic dipole polarizabilities $\alpha(i\omega)$ at imaginary frequencies of the two colliding species. If the collision involves a diatomic molecule, both the parallel and perpendicular components of the dynamic polarizability, $\alpha_{\parallel}(i\omega)$ and $\alpha_{\perp}(i\omega)$, need to be calculated.

Accurate values of $\alpha_{\parallel}(i\omega)$ and $\alpha_{\perp}(i\omega)$ for H_2 over a range of internuclear distances have been calculated by Ford and Browne [1] using a variational procedure [2]. They obtained $\bar{C}_6 = 12.09$ a.u. as the average of the H_2 - H_2 interaction C_6 coefficients over all the molecular orientations and all the internuclear distances in the lowest $v=0$ vibrational level. In a similar calculation at the equilibrium separation of the $v=0$ level at $R = 1.449a_0$, Bishop and Pipin [3] obtained $\bar{C}_6 = 12.06$ a.u. These results agree closely with the empirical values [4,5]. Thus there is little loss of accuracy in avoiding the vibrational averaging and using the dynamic polarizabilities evaluated at the equilibrium separation. Convenient representations of $\alpha_{\parallel}(i\omega)$ and $\alpha_{\perp}(i\omega)$ at $R = 1.449a_0$ have been constructed by Bishop and Pipin [3]. The possible error in the resulting values of C_6 is less than 1%.

Comparable high accuracy has been obtained for the dynamic polarizabilities of Li [6], and Na, K, Rb, Cs, and Fr [7]. The polarizabilities of Na, K, Rb, Cs, and Fr were obtained by an approximation of many-body perturbation theory [7].

II. CALCULATIONS

The leading term of the interaction energy at a large distance R between a spherical atom and a homonuclear diatomic molecule has the form

$$V(R) = -\frac{C_6}{R^6} [1 + \gamma P_2(\cos \theta)], \quad (1)$$

where $P_2(\cos \theta)$ is the second-order Legendre polynomial and θ is the angle between the symmetry axis of the mol-

ecule and the vector from the nucleus of the atom to the center of the molecule. The C_6 coefficient and anisotropy parameter γ can be expressed as

$$C_6 = \frac{1}{\pi} \left\{ \int_0^{\infty} \alpha_{\parallel}(i\omega) \alpha(i\omega) d\omega + 2 \int_0^{\infty} \alpha_{\perp}(i\omega) \alpha(i\omega) d\omega \right\} \quad (2)$$

and

$$\gamma = \frac{1}{\pi C_6} \left\{ \int_0^{\infty} \alpha_{\parallel}(i\omega) \alpha(i\omega) d\omega - \int_0^{\infty} \alpha_{\perp}(i\omega) \alpha(i\omega) d\omega \right\}, \quad (3)$$

where $\alpha_{\parallel}(i\omega)$ and $\alpha_{\perp}(i\omega)$ are, respectively, the parallel and the perpendicular dynamic dipole polarizabilities of H_2 and $\alpha(i\omega)$ is the dynamic dipole polarizability of an alkali-metal atom. We have plotted in Fig. 1 $\alpha_{\parallel}(i\omega)$ and $\alpha_{\perp}(i\omega)$ for H_2 , and $\alpha(i\omega)$ for Na as functions of the frequency ω , as an illustration.

The calculated values of C_6 and γ are compared in Table I with previous results of Victor and Dalgarno [4]. The values of γ agree closely. The differences in C_6 range from 0.3

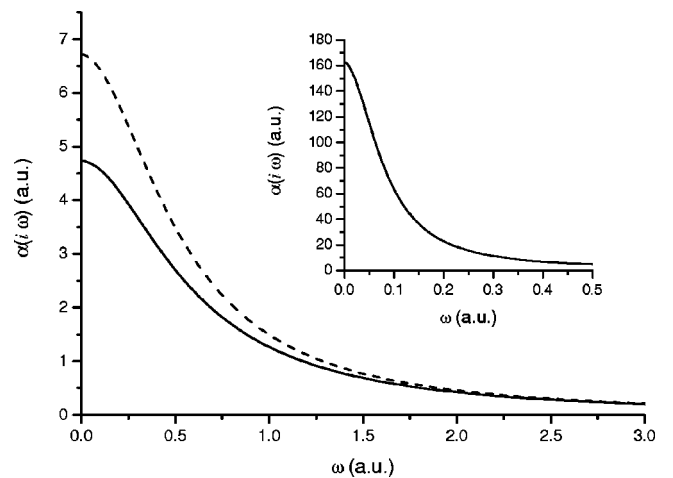


FIG. 1. Dynamic dipole polarizabilities of H_2 and Na as functions of the imaginary frequency ω . The solid and dashed curves denote the perpendicular and parallel components of the dynamic dipole polarizability of H_2 , $\alpha_{\perp}(i\omega)$ and $\alpha_{\parallel}(i\omega)$, respectively. The curve in the inset denotes the dynamic dipole polarizability of Na, $\alpha(i\omega)$.

TABLE I. C_6 coefficients and anisotropy parameters γ for interactions between molecular hydrogen and alkali-metal atoms.

Atom	C_6 [4]	C_6 (this paper)	γ [4]	γ (this paper)
Li	83.5	82.6	0.118	0.117
Na	92.0	92.3	0.118	0.116
K	127	139	0.120	0.116
Rb	136	156	0.120	0.115
Cs	160	189	0.120	0.114
Fr		181		0.113

for Na to 29 for Cs, reflecting the varying importance of the contribution, omitted by Victor and Dalgarno [4], of core transitions [8,7]. The values presented here are limited in accuracy because the method we have used does not allow

for the dependence of C_6 and γ on the rotational or vibrational population of the H_2 molecule. An estimate of the uncertainty in C_6 can be obtained from the calculations of Kolos and Wolniewicz [9] and of Ford and Browne [1] of the static dipole polarizability of H_2 for rotational levels $J=0-4$ of the $v=0$ vibrational level. The corresponding probable uncertainties for H_2 in the $v=0$ level interacting with the alkali-metal atoms are less than 2% for C_6 and still smaller for γ .

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