Van der Waals Forces between Copper and Noble-Gas Atoms

A. Bielski and J. Szudy

Institute of Physics, Nicholas Copernicus University,
Toruń, Poland

(Z. Naturforsch. **30 a**, 1203–1204 [1975] ;
received April 21, 1975)

The Van der Waals constants for the five lowest energy levels of CuI interacting with noble-gas atoms have been calculated using a semiempirical method. A comparison with the values obtained from the Coulomb approximation is presented.

Information on the interatomic potential is essential for the interpretaiton of many phenomena involving atom-atom collisions. The long range attractive potential between two atoms is usually represented by the Van der Waals potential $V(r) = -C_6 r^{-6}$, where r is the interatomic distance. Although the problem of calculating the constant C_6 has been the subject of many investigations, it is known for a few interacting atoms only. Most studies have been done for the interaction between alkali and noble-gas atoms [1–5]. This note reports the results of semiempirical evaluations of C_6 for the five lowest energy levels of copper interacting with noble-gas atoms.

Let us suppose that the atom A (e. g. Cu) is in the state described by the quantum numbers k, J, M $(k \equiv n, L)$, and the perturbing atom B (noble-gas atom) is in its ground state ${}^1S_0$. According to Margenau [6] and Fiutak and Frackowiak [7] the constant $C_6(k\,J\,M)$ may be written in the form

$$C_6(k\,J\,M) = \frac{\alpha I}{2} \sum_{k'J'M'} \frac{|\langle k\,J\,M\,|\,\mathbf{d}\,|\,k'\,J'\,M'\rangle|^2 + 3\,|\langle k\,J\,M\,|\,d_z\,|\,k'\,J'\,M'\rangle|^2}{E_{k'J'} - E_{kJ} + I} \tag{1}$$

where d_z is the z component of the dipole moment $\mathbf{d}$ of the atom A and α the polarizability of the atom B. $E_{k'J'}$ and E_{kJ} denote the energies of the levels $(k'\,J')$ and $(k\,J)$, respectively. The matrix elements in Eq. (1) are calculated in a rotating coordinate system where the z-axis is parallel to the line connecting the atoms A and B. Equation (1) has been derived from the general expression for C_6 assuming that the excitation energie ΔE_B of the noble gas atoms are nearly equal to the ionization energy I of the atom B. Applying the Eckart-Wigner theorem to the second term in the numerator of Eq. (1) we can transform it to the form

$$C_6(k\,J\,M) = \frac{\alpha I}{2(2J+1)} \sum_{k'J'} \frac{S(k\,J, k'\,J')}{E_{k'J'} - E_{kJ} + I} \left[1 + 3\,(1\,J'\,0\,M\,|\,J\,M)^2\right], \tag{2}$$

where $(1\,J'\,0\,M\,|\,J\,M)$ denotes the Clebsch-Gordan coefficient and $S(k\,J, k'\,J')$ is the line strength for the $(k\,J) \rightarrow (k'\,J')$ transition.

Equation (2) enables us to calculate the Van der Waals constant C_6 provided the line strengths are known. For CuI, however, there are no exact theo-

Table 1. Constants C_6 for CuI in units of 10^{-58} erg cm^6. SE — semiempirical values from Equation (2). CA — values obtained from the Coulomb approximation Equations (4) – (5).

State	$\|M\|$	He		Ne		Ar		Kr		Xe	
		SE	CA	SE	CA	SE	CA	SE	CA	SE	CA
$3d^{10}4s\ {}^2S_{1/2}$	1/2	0.103	0.100	0.185	0.185	0.717	0.679	1.06	0.973	1.66	1.52
$3d^{10}4p\ {}^2P_{1/2}$	1/2	0.308	0.26	0.563	0.503	2.27	2.01	3.43	2.98	5.50	4.80
$3d^{10}4p\ {}^2P_{3/2}$	1/2	0.407	0.323	0.746	0.624	3.01	2.51	4.56	3.74	7.33	6.04
	3/2	0.253	0.209	0.462	0.403	1.85	1.6	2.79	2.35	4.45	3.78
$3d^94s^2\ {}^2D_{3/2}$	1/2	0.00404	—	0.00733	—	0.0288	—	0.0429	—	0.0675	—
	3/2	0.00305	—	0.00553	—	0.0216	—	0.0321	—	0.0505	—
$3d^94s^2\ {}^2D_{5/2}$	1/2	0.00744	—	0.0134	—	0.0518	—	0.0768	—	0.1199	—
	3/2	0.00609	—	0.0110	—	0.0424	—	0.0629	—	0.0982	—
	5/2	0.00349	—	0.00631	—	0.0244	—	0.0361	—	0.0564	—

Reprint requests to Dr. A. Bielski, Institute of Physics, Nicholas Copernicus University, Grudziadzka 5, *87-100 Toruń*, Poland.

retical data of $S(k\,J, k'\,J')$. Therefore, in the present study we have calculated the line strengths for CuI from the experimental transition probabilities taken from a recent critical review of existing experimental data[8]. The following five energy levels of CuI were considered: $3d^{10}\,4s\,{}^2S_{1/2}$, $3d^{10}\,4p\,{}^2P_{1/2,3/2}$ and $3d^9\,4s^2\,{}^2D_{3/2,5/2}$. The values of C_6 computed from Eq. (2) for the interaction of Cu with noble-gas atoms are shown in Table 1. We have used the following experimental values for noble-gas polarizabilities[9] (in units of $10^{-24}\,\mathrm{cm}^3$): 0.216 – He, 0.398 – Ne, 1.63 – Ar, 2.48 – Kr, 4.01 – Xe. They do not differ significantly from the theoretical values of Dalgarno and Kingston[10]: 0.205, 0.395, 1.64, 2.48, 4.04 for He, Ne, Ar, Kr and Xe atoms, respectively.

The only previously reported data of the constants C_6 for CuI are those of Miyachi and JayaRam[11] for the $3d^{10}\,4p\,{}^2P_{1/2,3/2}$ levels for the interaction with argon atoms. Their calculations are based on the Mahan method[4, 5] in which a Coulomb approximation of the Bates-Damgaard[12] type is used for the calculation of the radial matrix elements. The basic assumption of Mahan's method is the expansion:

$$(\Delta E_A + \Delta E_B)^{-1} = \Delta E_A^{-1} - \Delta E_A\, \Delta E_B^{-2} + \dots$$

which is valid provided $\Delta E_A \ll \Delta E_B$. Here ΔE_A denotes the excitation energy of the atom A.

In order to compare our semiempirical values of the Van der Waals constants with those obtained from the Coulomb approximation we also have calculated C_6 for the $3d^{10}\,4s\,{}^2S_{1/2}$ and $3d^{10}\,4p\,{}^2P_{1/2,3/2}$ states of CuI interacting with all noble-gas atoms using the expressions given by Mahan.

According to Mahan[5] the constant $C_6(k\,J\,M)$ can be written as the sum of two terms

$$C_6(k\,J\,M) = C_6^{(0)}(k\,J\,M) + C_6^{(1)}, \tag{3}$$

where the second term $C_6^{(1)}$ depends only on the noble-gas atom and the first term $C_6^{(0)}(k\,J\,M)$ is a linear combination of constants $C_6^{(6)}(n\,L\,M_L)$ corresponding to quantum numbers $n\,L\,M_L$:

$$C_6^{(0)}(k\,J\,M) = \sum_{M_L} a_{M_L}\, C_6^{(0)}(n\,L\,M_L). \tag{4}$$

The values of the coefficient a_{M_L} as well as $C_6^{(1)}$ are listed in the paper of Mahan[5]. In the Coulomb approximation, $C_6^{(0)}(n\,L\,M_L)$ is given by

$$C_6^{(0)}(n\,L\,M_L) = \tfrac{1}{2}\, e^2 a_B^2\, \alpha (n^*)^2 \cdot \frac{[5(n^*)^2 + 1 - 3\,L(L+1)]\,[5\,L(L+1) - 3(M_L^2+1)]}{(2\,L+3)\,(2\,L-1)} \tag{5}$$

where e is the electronic charge, a_B the Bohr radius and n^* the effective quantum number.

The values C_6 calculated from Eqs. (4) – (5) are shown in Table 1. For the $3d^9\,4s^2\,{}^2D_{3/2,5/2}$ states the Coulomb approximation cannot be applied because it assumes one electron outside closed shells. The formal application of Eq. (5) for these states yields negative values of C_6.

As can be seen in Table 1 there is reasonable agreement between the semiempirical values of the constants C_6 obtained from Eq. (2) with those theoretically determined from the Mahan expression for the $3d^{10}\,4s\,{}^2S_{1/2}$ and $3d^{10}\,4p\,{}^2P_{1/2,3/2}$ states.

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