Long-range interaction of two metastable rare-gas atoms

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(Received 30 May 2000; published 27 October 2000)

We present semiempirical calculations of long-range van der Waals interactions for two interacting metastable rare-gas atoms Ne through Xe. Dispersion coefficients C_6 are obtained for homonuclear molecular potentials asymptotically connecting to the $ns(3/2)_2 + ns(3/2)_2$ atomic states. The estimated uncertainty of the calculated C_6 dispersion coefficients is 4%.

PACS number(s): 32.10.Dk, 34.20.−b, 32.70.Cs

Motivated by cold-collision studies of metastable rare-gas atoms [1–4] and prospects of achieving Bose-Einstein condensation in these systems [5], we present calculations of long-range dispersion (van der Waals) coefficients for two atoms interacting in the $ns(3/2)_2$ atomic states ($n=3$ for Ne, $n=4$ for Ar, $n=5$ for Kr, and $n=6$ for Xe). The metastable states have long lifetimes, 43 s for Xe [6], decaying to the ground $^1S_0$ state by a weak magnetic-quadrupole transition. With such a long lifetime the metastable atom behaves as an effective ground state in experiments. Compared to alkali-metal systems, an attractive feature of the noble-gas atoms is the availability of isotopes with zero nuclear spin. The lack of hyperfine structure leads to a substantial simplification of molecular potentials, though some complexity arises due to the nonvanishing total electron angular momentum ($J=2$) of the metastable state. The anisotropy leads to 15 distinct long-range molecular states connecting to the $ns(3/2)_2 + ns(3/2)_2$ asymptotic configuration.

Our theoretical treatment of long-range interactions is similar to recent high-precision calculations of van der Waals coefficients for alkali-metal atoms [7]. By using many-body methods and accurate experimental matrix elements for the principal transitions, leading dispersion coefficients C_6 were determined to an accuracy better than 1% for Na, K, and Rb, and of 1% for Cs and 1.5% for Fr. The *semiempirical* values of C_6 coefficients for metastable noble-gas atoms obtained here have an estimated uncertainty of 4%. The approach relies on the determination of dynamic polarizability functions. To construct the polarizabilities we combine experimental lifetime [8–15] and energy data of the excited states with accurate semiempirical dynamic polarizabilities of the ground states of noble-gas atoms [16]. The theoretical lifetimes and branching ratios [17] are adjusted to reproduce the measured static polarizabilities [18], which are known with a 2% uncertainty. We estimated the additional small contributions within the Dirac-Hartree-Fock framework. The resulting polarizabilities satisfy the Thomas-Reiche-Kuhn (TRK) oscillator strength sum rule.

The Racah notation for atomic levels is used. The particle-hole states are labeled as $nl(K)_J$ or $nl'(K)_J$, where n and l are the principal and the orbital angular momentum quantum numbers of the valence electron and $\mathbf{K}=\mathbf{J}_c+l$, where J_c is the angular momentum of the core. The primed configurations converge to a Rydberg series limit with a hole in the $(n-1)p_{1/2}$ state, and the unprimed to a hole in the $(n-1)p_{3/2}$ state. The manifold of the lowest ns valence states has four fine-structure states $ns'(1/2)_{0,1}$ and $ns(3/2)_{1,2}$, and the lowest np manifold consists of ten states. We investigate here the molecular potentials asymptotically connecting to the $ns(3/2)_2$ atomic states.

We calculate the long-range molecular potentials in the framework of Rayleigh-Schrödinger perturbation theory. The basis functions are defined as products of atomic wave functions

$$|M_1 M_2; \Omega\rangle = |ns(3/2)_2 M_1\rangle_1 |ns(3/2)_2 M_2\rangle_2, \quad (1)$$

where the index 1(2) describes the wave function located on the center 1(2) and $\Omega = M_1 + M_2$, $M_{1,2}$ being projections of the atomic total angular momentum on the internuclear axis. Due to the axial symmetry of a dimer, Ω is a conserved quantum number. It takes values ranging from zero to four. The two-atom basis (1) is degenerate and the correct molecular wave functions are obtained by diagonalizing the molecular Hamiltonian

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{V}(R). \quad (2)$$

In expression (2) $\hat{H}_k$ represent the Hamiltonians of the two noninteracting atoms, and $\hat{V}(R)$ is the interaction potential at an internuclear distance R. The energy of the $ns(3/2)_2$ metastable state is designated as $\mathcal{E}^*$. Then in the model space (1):

$$(\hat{H}_1 + \hat{H}_2)|M_1 M_2; \Omega\rangle = 2\mathcal{E}^* |M_1 M_2; \Omega\rangle.$$

The residual electrostatic potential $\hat{V}(R)$ is defined as the full Coulomb interaction energy in the dimer excluding interactions of the atomic electrons with their parent nuclei.

The multipole interactions ($L=1$ for dipole-dipole, and $L=2$ for quadrupole-quadrupole interactions) are given by [19]

$$V_{LL}(R) = \frac{1}{R^{2L+1}} \sum_{\mu=-L}^{L} \frac{(2L)!}{(L-\mu)!(L+\mu)!} (T_\mu^{(L)})_1 (T_{-\mu}^{(L)})_2, \quad (3)$$

with the multipole spherical tensors

$$T_\mu^{(L)} = -|e| \sum_i r_i^L C_\mu^{(L)}(\hat{\mathbf{r}}_i), \quad (4)$$

where the summation is over atomic electrons, $\mathbf{r}_i$ is the position vector of electron i, and $C_\mu^{(L)}(\hat{\mathbf{r}}_i)$ are normalized spherical harmonics [20]. In the following we write $d_\mu = T_\mu^{(1)}$ and $Q_\mu = T_\mu^{(2)}$.

The lowest-order contribution to the term energies arises from the quadrupole-quadrupole interaction $\hat{V}_{qq}$, which varies as $1/R^5$. However, the corresponding C_5 coefficients are only of the order $10^1 - 10^2$ a.u. [2], and the dominant contribution appears in the second order in $\hat{V}(R)$, arising from the dipole-dipole interaction $\hat{V}_{dd}$. The second-order dipole interaction is proportional to $1/R^6$, and the associated dispersion coefficient C_6 is of the order of $10^4 - 10^5$ a.u. Applying the formalism of degenerate perturbation theory in second order [21], we obtain an effective Hamiltonian within the two-atom basis Eq. (1):

$$\langle m|H_{\mathrm{eff}}^{(2)}|n\rangle = 2\mathcal{E}^*\delta_{mn} + \langle m|\hat{V}_{qq}|n\rangle$$
$$+ \sum_{\Psi_i} \frac{\langle m|\hat{V}_{dd}|\Psi_i\rangle\langle\Psi_i|\hat{V}_{dd}|n\rangle}{2\mathcal{E}^* - E_i}. \qquad (5)$$

The intermediate molecular state $|\Psi_i\rangle$ with unperturbed energy E_i runs over a *complete* set of two-atom states, excluding the model-space states Eq. (1). The formalism of the generalized Bloch equation [22] would allow the inclusion in the model space of the other three atomic states in the ns manifold and would account for the mixing of the different fine-structure levels; but such a large model space is not necessary for $R > 10$ a.u. The position of the avoided level crossing can be estimated from $R_{l.c.} \approx 2C_6/(\mathcal{E}_{ns(3/2)_1} - \mathcal{E}_{ns(3/2)_2}) \sim 10$ a.u. The $\Omega = 4$ molecular term is unique and being unaffected by avoided crossings, the region of applicability is extended to $R \sim n$ a.u., before the electronic clouds start to overlap. The effect of the quadrupole-quadrupole interaction on the term energy can be disregarded at values of $R \ll C_6/C_5 \sim 10^3$ a.u. The quadrupole-quadrupole correction is discussed by Doery *et al.* [3].

Using the Wigner-Eckart theorem, we can represent the matrix element of the dipole-dipole term in the effective second-order Hamiltonian as

$$\sum_{\Psi_i} \frac{\langle M_1 M_2;\Omega|\hat{V}_{dd}|\Psi_i\rangle\langle\Psi_i|\hat{V}_{dd}|M_1' M_2';\Omega\rangle}{2\mathcal{E}^* - E_i}$$

$$= -\frac{1}{R^6}\sum_{II'} C_6^{J_a J_b}(-1)^{J_a + J_b}\frac{2}{3}$$

$$\times \sum_{\lambda\mu} w_\lambda^1 w_\mu^1 \mathcal{A}_{\lambda\mu}^{J_a}(M_1, M_1')$$

$$\times \mathcal{A}_{-\lambda-\mu}^{J_b}(\Omega - M_1, \Omega - M_1'). \qquad (6)$$

The dipole weights w_μ^1 are $w_{+1}^1 = w_{-1}^1 = 1$, and $w_0^1 = 2$. J_a and J_b are the corresponding total angular momenta of intermediate atomic states of atoms 1 and 2, and

$$\mathcal{A}_{\lambda\mu}^I(M_1, M_1') = \begin{pmatrix} 2 & 1 & I \\ -M_1 & \mu & m \end{pmatrix}\begin{pmatrix} I & 1 & 2 \\ -m & \lambda & M_1' \end{pmatrix}, \qquad (7)$$

where $m = \frac{1}{2}(M_1 + M_1' + \lambda - \mu)$. The intermediate (uncoupled) dispersion coefficients are

$$C_6^{J_a J_b} = \frac{3}{\pi}\int_0^\infty d\omega\, S_{J_a}(i\omega)S_{J_b}(i\omega). \qquad (8)$$

The reduced dynamic dipole polarizability $S_I(i\omega)$ of purely imaginary argument is defined as the sum over atomic states $|\alpha_I I M_I\rangle$ with total angular momentum I and energy $\mathcal{E}_{\alpha_I}$:

$$S_I(i\omega)$$
$$= \sum_{\alpha_I} \frac{(\mathcal{E}^* - \mathcal{E}_{\alpha_I})\langle ns(3/2)_2||d||\alpha_I I\rangle\langle\alpha_I I||d||ns(3/2)_2\rangle}{(\mathcal{E}^* - \mathcal{E}_{\alpha_I})^2 + \omega^2}. \qquad (9)$$

Here α_I stands for all quantum numbers of the intermediate state, except for the total angular momentum I, and $\langle i||d||j\rangle$ are the reduced electric-dipole matrix elements, defined by the Wigner-Eckart theorem. Three sums with $I = 1,2,3$ are allowed by electric-dipole selection rules.

We proceed now to construct the dipole polarizability functions $S_I(i\omega)$, Eq. (9), evaluate the uncoupled dispersion coefficients (8), and set and diagonalize the second-order effective Hamiltonian (5).

The functions $S_I(i\omega)$ satisfy several sum rules. In particular, the static tensor dipole polarizability $\alpha_{zz}(M)$ of the $ns(3/2)_2$ state may be expressed as

$$\alpha_{zz}(M) = -2\sum_I (-1)^I \begin{pmatrix} 2 & 1 & I \\ -M & 0 & M \end{pmatrix}^2 \times S_I(0). \qquad (10)$$

The static tensor dipole polarizabilities $\alpha_{zz}(M=1)$ and $\alpha_{zz}(M=2)$ of metastable noble-gas atoms Ne through Xe have been measured by Molof *et al.* [18] to within an error of 2%. In the present calculations the values of $S_I(0)$ are adjusted to reproduce these experimental values. In addition, as $\omega \to \infty$, the reduced polarizabilities satisfy the nonrelativistic TRK sum rule

$$\sum_n f_{kn} = \frac{2}{15}\sum_I (-1)^{I+1} S_I(i\infty) = N, \qquad (11)$$

N being the number of electrons in the atom. Our constructed polarizabilities satisfy the sum rule.

It is instructive to consider the action of a one-particle operator on the reference particle-hole Slater determinant $ns(3/2)_2$ in the independent electron approximation. Such an operator can (i) annihilate the reference particle-hole pair; (ii) promote a valence electron from the $ns_{1/2}$ state to another valence state $mp_{1/2,3/2}$, the state of the $(n-1)p_{3/2}$ hole being unchanged; (iii) de-excite the $(n-1)p_{3/2}$ hole into some other hole state, the valence state remaining the same, and (iv) create another particle-hole pair in addition to the refer-

ence pair. According to such a classification it is convenient to break the polarizability function, Eq. (9), into three contributions S_I^k corresponding to a number k of particle-hole pairs in the intermediate state $|\alpha_I I\rangle$:

$$S_I = S_I^0 + S_I^1 + S_I^2.$$

Since an electric-dipole transition from $ns(3/2)_2$ to the closed-core state $^1S_0$ is prohibited by the angular selection rules, $S_I^0 \equiv 0$.

The sum S_I^1 is separated into contributions from the intermediate states in the lowest np fine-structure multiplet $(S_I^1)_{np}$, and the rest of the sum $(S_I^1)'$:

$$S_I^1 = (S_I^1)_{np} + (S_I^1)'.$$

The first term is the dominant contribution. We calculate $(S_I^1)_{np}$ using experimental values of transition energies and decay rates, and adjusted branching ratios. The rest of the sum over valence states (including bound and continuum states) $(S_I^1)'$ is estimated in the Dirac-Hartree-Fock (DHF) approximation. The metastable state $|vh;J\rangle$ in lowest order is represented as a combination of the $|v\rangle = ns_{1/2}$ particle state and the hole state $|h\rangle = (n-1)p_{3/2}$, coupled to the total angular momentum $J=2$, $\{[(n-1)p_{3/2}]^{-1}ns_{1/2}\}_2$. The lowest-order energy of such a state is $\mathcal{E}^* = \varepsilon_v - \varepsilon_h$, ε_i being the energy of the DHF orbital $|i\rangle$. The intermediate state is represented as $|ma;I\rangle$, a particle state m coupled with hole state a to the total momentum I. Explicitly,

$$(S_I^1)'(i\omega) = (-1)^{J+I}[I][J]$$

$$\times \sum_{ma}' \left(\delta_{ha} \frac{(\varepsilon_v - \varepsilon_m)\langle v||d||m\rangle^2}{(\varepsilon_v - \varepsilon_m)^2 + \omega^2} \right.$$

$$\times \begin{Bmatrix} J & 1 & I \\ j_m & j_h & j_v \end{Bmatrix}^2 + \delta_{mv} \frac{(\varepsilon_a - \varepsilon_h)\langle h||d||a\rangle^2}{(\varepsilon_a - \varepsilon_h)^2 + \omega^2}$$

$$\left. \times \begin{Bmatrix} J & 1 & I \\ j_a & j_v & j_h \end{Bmatrix}^2 \right),$$

where $[K] \equiv 2K+1$, the summation is performed over the core orbitals a and excited states m, excluding states of the lowest np multiplet, and $J=2$. The first sum is associated with excitation of the valence electron [case (ii)] while the second sum with de-excitation of the hole state [case (iii)]. To arrive at this result we disregarded the coupling between levels within the same fine-structure multiplet. For example, for Ne the $[(2p_{3/2})^{-1}4p_{1/2}]_2$, $[(2p_{3/2})^{-1}4p_{3/2}]_2$, and $[(2p_{1/2})^{-1}4p_{3/2}]_2$ states are summed over independently, even though the correct lowest-order wave function is a linear combination of them. This approximation corresponds to a disregard of the small difference between the energies of the coupled and uncoupled states. Since the contribution $(S_I^1)'$ is relatively small, such an estimate suffices at the present level of accuracy. Numerical evaluation of $(S_I^1)'$ has been performed using a B-spline basis set in the V_{N-1} DHF potential, with the hole in the $(n-1)p_{3/2}$ core orbital [23].

The calculated term $(S_I^1)'(\omega=0)$ typically contributes at the 1% level to the reduced sums $S_I(0)$ for all the systems we consider.

We separate the sum S_I^2 over the core excited states into two contributions:

$$S_I^2 = (S_I^2)_{\text{core}} + (S_I^2)_{\text{cntr}}.$$

The first term is associated with the dynamic polarizability $\alpha_g(i\omega)$ of the closed-shell ground state $^1S_0$ and the second term is a corrective counter term.

$$(S_I^2)_{\text{core}}(i\omega) = (-1)^{I+J+1}\frac{[I]}{2}\alpha_g(i\omega). \qquad (12)$$

We use the semiempirical dynamic polarizabilities for the ground states of noble-gas atoms of Kumar and Meath [16]. The estimated uncertainty of these core polarizabilities is less than 1%. The primary role of the core polarizability is to provide the correct limit [Eq. (11)] at $\omega \to \infty$. The relative importance of the core-excitation contribution increases for heavier systems; for example, in a similar calculation for Fr [7], core excitations contribute 23% of the C_6 dispersion coefficient. The high-frequency limit, Eq. (11), is accurately reproduced by the present *total* reduced dynamic polarizabilities $S_I(i\omega)$. We obtain for Ne 9.98, for Ar 17.95, for Kr 35.95, and for Xe 53.96 compared to the nonrelativistically exact values 10, 18, 36, and 54, respectively.

In the $ns(3/2)_2 = \{[(n-1)p_{3/2}]^{-1}ns_{1/2}\}_2$ state core excitations to the occupied magnetic substates of the $ns_{1/2}$ particle state are not allowed by the Pauli exclusion principle, and neither are the core excitations from the empty magnetic substate of the hole $(n-1)p_{3/2}$. To remove these transitions from the core polarizability contribution $(S_I^2)_{\text{core}}$, we introduce a counter term $(S_I^2)_{\text{cntr}}$. Explicitly in the independent-electron model

$$(S_I^2)_{\text{cntr}}(i\omega) = [I][J](-1)^{I+J}$$

$$\times \left(\sum_a \frac{(\varepsilon_v - \varepsilon_a)\langle a||d||v\rangle^2}{(\varepsilon_v - \varepsilon_a)^2 + \omega^2} \begin{Bmatrix} 1 & J & I \\ j_h & j_a & j_v \end{Bmatrix}^2 \right.$$

$$\left. + \sum_m \frac{(\varepsilon_m - \varepsilon_h)\langle h||d||m\rangle^2}{(\varepsilon_m - \varepsilon_h)^2 + \omega^2} \begin{Bmatrix} 1 & J & I \\ j_v & j_m & j_h \end{Bmatrix}^2 \right).$$

We estimate the counterterm using the Dirac-Hartree-Fock approximation. This term typically contributes less than 1% to the total $S_I(i\omega)$.

The largest contribution to the sums S_I arises from the intermediate states in the lowest np fine-structure multiplet. The determination of electric-dipole matrix elements involved in the sum $(S_I^1)_{np}$ requires a knowledge of both decay rates and branching ratios in the manifold. The relevant lifetimes have been measured to within an error less than 1% for Ne [8,9], Ar [10], and Kr [11], and less than 3% for Xe [12–14]. However, the branching ratios B are not established to the same precision. The most accurate measurements of B in Ne [8,9], have an error bar of approximately 4%–5%, which would introduce an uncertainty of 4%–5% in the

TABLE I. Input data for Ar and Xe calculations. Lifetimes τ for Ar are from Volz and Schmoranzer, Ref. [10], and for Xe from Inoue *et al.*, Ref. [12], except where noted. Branching ratios B to the $ns(3/2)_2$ level are adjusted to reproduce experimental tensor dipole polarizabilities, as discussed in the text.

State	Ar, $n=4$ τ, ns	$B(\%)$	Xe, $n=6$ τ, ns	$B(\%)$
$np'(1/2)_1$	27.85(7)	17.66	43.5(1.5)[b]	5.15
$np'(3/2)_2$	29.01(7)	10.59	38.1(1.3)[c]	2.30
$np'(3/2)_1$	29.83(8)	1.84	49(2)	1.16
$np(3/2)_2$	28.52(7)	68.55	31(1)	65.42
$np(3/2)_1$	29.62(7)	14.97	37(1)	7.45
$np(5/2)_2$	31.17(7)	27.76	39(1)	33.29
$np(5/2)_3$	29.00(7)	100.00	31(1)	100.00
$np(1/2)_1$	39.2(2.2)[c]	72.11	38(1)	87.60

[a]Allen *et al.*, Ref. [14].
[b]Husson and Margerie, Ref. [13].
[c]Wiese *et al.*, Ref. [15].

static polarizabilities, and 8%–10% inaccuracy in the values of C_6. To reduce the consequent errors, the experimental values of the static polarizability, accurate to 2%, were chosen as the reference data.

The branching ratios of transitions to the $ns(3/2)_2$ state have been adjusted as follows. The sum $S_3(0)$ includes only one intermediate state in the np manifold, $np(5/2)_3$, and very small *ab initio* corrections. The $np(5/2)_3$ state has a single decay channel, so that the sum $S_3(0)$ is known with the experimental precision of the decay rate. The sums $S_2(0)$ and $S_1(0)$ can be deduced from the experimental values of the static tensor polarizability as

$$S_1(0) = -\tfrac{9}{14}S_3(0) + 5\,\alpha_{zz}(1) - \tfrac{5}{4}\,\alpha_{zz}(2),$$

$$S_2(0) = \tfrac{5}{14}S_3(0) - \tfrac{15}{4}\alpha_{zz}(2).$$

Removing small *ab initio* and semiempirical core-excitation contributions from these sums, the sums $(S_1^1)_{np}(0)$ and $(S_2^1)_{np}(0)$ are obtained. The branching ratios B for four states involved in the $J=1$ sum and three states in the $J=2$ sum were multiplied by a uniform scaling factor. Branching ratios for Ne [8] for the $J=1$ levels were multiplied by 1.0035, and for the $J=2$ level by 0.905 in order to reproduce the experimental values of the static tensor polarizabilities. We modified the recommended values of B for Ar [15] by multiplying the branching ratios of the $J=1$ states by 0.973 and of the $J=2$ states by 0.965; the values used in the calculations are listed in Table I. For Kr the velocity-gauge branching ratios, tabulated in Ref. [2] from calculations by Aymar and Coulombe [17], were multiplied by 1.127 for the $J=1$ states and by 1.0016 for the $J=2$ states. For Xe, velocity-gauge values of B calculated in Ref. [17] were multiplied by 0.927 for the $J=1$ states and by 0.929 for the $J=2$ states. The adjusted data for Ar and Xe are listed in Table I. Doery *et al.* [2] have compiled the input data for Ne and Kr, which have to be similarly modified.

TABLE II. Intermediate dispersion coefficients $C_6^{J_a J_b}$, a.u., multiplied by a factor 10^{-3}.

	C_6^{11}	C_6^{21}	C_6^{22}	C_6^{31}	C_6^{32}	C_6^{33}
Ne	4.945	−7.333	10.89	10.92	−16.21	24.14
Ar	12.48	−17.42	24.39	27.12	−37.88	59.02
Kr	15.12	−20.18	27.01	31.80	−42.44	66.96
Xe	23.24	−29.22	36.91	47.74	−60.06	98.31

We employ the constructed reduced polarizabilities $S_l(i\omega)$ to calculate the intermediate uncoupled dispersion coefficients $C_6^{J_a J_b}$ by quadrature using Eq. (8). The coefficients are listed in Table II. They are to be used if the entire molecular Hamiltonian, including quadrupole-quadrupole and higher multipoles or perturbation-theory orders is to be diagonalized. Finally, the molecular terms are obtained by the diagonalization of $H_{\text{eff}}^{(2)}$, given by Eq. (5). Neglect of the small corrections due to the quadrupole-quadrupole interaction results in parameterization of term energies in the form

$$U(R) = 2\mathcal{E}^* - C_6/R^6.$$

The calculated dispersion coefficients C_6 for various molecular symmetries are listed in Table III. Since the region close to $\omega=0$ contributes the most to the values of the integral in Eq. (8), the uncertainty in the values of C_6 is approximately 4%, reflecting the 2% experimental error in the static dipole tensor polarizabilities [18]. The values of the C_6 coefficients grow monotonically from Ne to Xe, due to the reduction in the energy separations between the metastable states and the np manifold. For heavier systems the anisotropy in C_6, arising from relativistic effects, becomes increasingly marked, from 6.5% in Ne to 16% in Xe.

Long-range dispersion coefficients for two interacting metastable Ne atoms were evaluated recently by Doery *et al.* [3] The C_6 coefficients were calculated from the diagonal-

TABLE III. Dispersion coefficients C_6 in a.u. for the interaction of two metastable $ns(3/2)_2$ noble-gas atoms.

Term	Ne	Ar	Kr	Xe
4_g	1877	4417	4994	7138
3_g	1919	4565	5195	7490
3_u	1922	4583	5224	7557
2_g	1967	4751	5459	7991
2_g	1935	4629	5286	7664
2_u	1934	4623	5276	7641
1_u	1983	4811	5543	8148
1_g	1982	4810	5541	8145
1_g	1920	4574	5210	7524
1_u	1920	4574	5210	7526
0_g^+	1999	4872	5629	8311
0_g^+	1968	4756	5467	8010
0_u^-	1966	4747	5452	7975
0_u^-	1877	4418	4996	7140
0_g^+	1877	4418	4996	7140

ization of the molecular dipole-dipole Hamiltonian in the model space containing the lowest np manifold, so limiting the intermediate states to the lowest np-manifold states in the present formulation. Experimental values of decay rates and branching ratios were used to deduce the electric-dipole matrix elements. The precision of the calculated values of C_6 is about 8%–10% due to the large uncertainty in the branching ratios. The values of C_6 from Ref. [3] for different molecular symmetries vary between 1951 and 1956 a.u., exhibiting much less anisotropy than the present results that range between 1877 and 1999 a.u. The difference can be traced to the anisotropy in the static dipole polarizabilities. Indeed, utilizing input data from Ref. [3] we obtain $\alpha_{zz}(M=1) = 192$ and $\alpha_{zz}(M=2) = 189$ a.u. if we include only the np manifold as in Ref. [3]. While $\alpha_{zz}(M=1)$ agrees with the experimental value [18] 192(4), the $\alpha_{zz}(M=2)$ is overestimated by three standard deviations compared to the experimental value 180(3) a.u.

The accuracy of the dispersion coefficients could be improved by applying relativistic all-order many-body methods [23,24] to calculate transition amplitudes between $ns-np$ manifolds. Such *ab initio* calculations are intrinsically more challenging than for alkali-metal atoms; the accurate experimental lifetimes would provide an excellent gauge of accuracy.

Our values of C_6 coefficients will be useful in studies of cold collisions of metastable rare-gas atoms [1–4]. In the limit of high temperatures, we can estimate the rate coefficient for Penning ionization by ignoring spin polarization and assuming that every trajectory that surmounts the angular momentum barrier leads to ionization [1,25]. The corresponding rate coefficient is given by [25]

$$k = 6.35 \times 10^{-9} \frac{C_6^{1/3} T^{1/6}}{\mu^{1/2}} \, \text{cm}^3 \, \text{s}^{-1},$$

where μ is the reduced mass measured in units of the electron mass and T is the temperature. At ultralow temperatures, the s-wave scattering becomes dominant and the Penning ionization rate becomes independent of the temperature [1].

Combined with short-range potentials [3,26] a number of other properties could be determined. For example, scattering lengths of elastic collisions could be found, providing input for mean-field equations describing dilute quantum gases.

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