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Coulomb-stable triply charged diatomic: HeY^{3+}

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Accurate relativistic coupled-cluster calculations show that the triply charged species HeY^{3+} is a stable molecule and represents the lightest diatomic trication that does not undergo a Coulomb fragmentation into charged fragments. The diatomic potential-energy curve is approximated by an extended Morse potential, and vibrational-rotational constants for HeY^{3+} are predicted ($R_e = 224.3\,\text{pm}$, $D_0 = 0.394\,\text{eV}$, $\omega_e = 437\,\text{cm}^{-1}$, $\omega_e x_e = 15.8\,\text{cm}^{-1}$, $B_e = 0.877\,\text{cm}^{-1}$). It is further shown that the He—Y^{3+} bond can basically be described as a charge-induced dipole interaction. [S1050-2947(99)50711-7]

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The investigation of multiply charged diatomic cations represents a challenging task. Already for doubly charged diatomic compounds most potential curves are repulsive; thus the XY^{2+} species undergo a Coulomb fragmentation with $X^{+} + Y^{+}$ as the dissociation limit [1,2]. Triply charged diatomic compounds are even more elusive and generally occur in metastable states only, i.e., in local minima on excited potential curves *above* the positively charged fragments [3]. For example, Sakai *et al.* could recently generate the metastable halogen trications Cl_2^{3+}, Br_2^{3+}, and I_2^{3+} by femtosecond pulse strong-field multiphoton ionization [4]. The search for *stable* triply charged diatomics so far has focused on the rare-earth or actinide series, as these elements exhibit low ionization potentials. These heavy metals are in general combined with helium, which has the highest first ionization potential of all elements ($V_{\mathrm{IP}_0} = 24.59\,\text{eV}$) [5] or with other hardly ionizable atoms [6–9]. For elements E other than the f elements there is no evidence so far that a Coulomb stable helide HeE^{3+} can exist (we define as Coulomb stable if any of the dissociation limits $He^{n+} + E^{+3-n}$, $n = 0$, 1, and 2, lie above the HeE^{3+} minimum) [3,6,10].

The lightest element in the periodic table that has a third ionization potential V_{IP_2} ($E^{2+} \rightarrow E^{3+}$) smaller than the first ionization potential of He is yttrium [6] (Table I). It is therefore likely that HeY^{3+} forms a stable species, and the curve crossing between the repulsive $He^{+} + Y^{2+}$ and the bound $He + Y^{3+}$ potential curves does not occur. We investigated the Born-Oppenheimer (BO) potential-energy curve $V(R)$ for the $He + Y^{3+}$ system at the Douglas-Kroll (DK) [11] relativistic coupled-cluster level [CCSD(T)] [12], using very large Gaussian-type basis sets (Gaussian-type orbital) [13] of Hartree-Fock (HF) limit quality [14–16]. The atomic results are shown in Table I, and the good agreement with available experimental data demonstrates the quality of the employed basis sets and methods. The calculated potential-energy curve is shown in Fig. 1; spectroscopic constants derived from a numerical Numerov-Cooley procedure [17] are listed in Table II.

The results show that HeY^{3+} represents the lightest stable triply charged diatomic molecule. Its dissociation energy D_e compared to the $He + Y^{3+}$ exit channel amounts to 0.42 eV, and Coulomb fragmentation into the charged fragments $He^{+} + Y^{2+}$ is endothermic by 4.7 eV. This does not preclude

TABLE I. Atomic ionization potentials for He and Y. All values are in eV. The fourth ionization potential is defined by $Y^{3+}(^1S_0) \rightarrow Y^{4+}(^2P_{3/2})$. Identical contraction schemes but different contraction coefficients have been used in the nonrelativistic (NR) and Douglas-Kroll (DK) calculations. num. stands for numerical; alg, stands for algebraic calculations.

	NRHF (num.)	NRHF (alg.)	NRCCSD(T) (alg.)	DHF (num.)	DKHF (alg.)	DKCCSD(T) (alg.)	Expt.[a]
$He(^1S_0)$	23.448	23.448	24.564	23.448	23.448	24.564	24.580
$He^{+}(^2S_{1/2})$	54.423	54.418	54.418	54.426	54.420	54.420	54.400
$Y(^2D_{3/2})$	5.749	5.896	6.320	5.355	[b]	[b]	6.5
$Y^{+}(^1S_0)$	10.402	10.278	11.627	11.132	11.111	11.800	12.4
$Y^{2+}(^2D_{3/2})$	19.889	19.998	20.470	19.613	19.603	20.294	20.5
$Y^{3+}(^1S_0)$	59.833	59.617	60.520	59.505	59.967	60.889	

[a] Experimental values from Ref. [5].

[b] No first VIP can be given since the ROHF scheme implemented in MOLCAS3 yields an incorrect description of the valence d orbital in Y^{0}.

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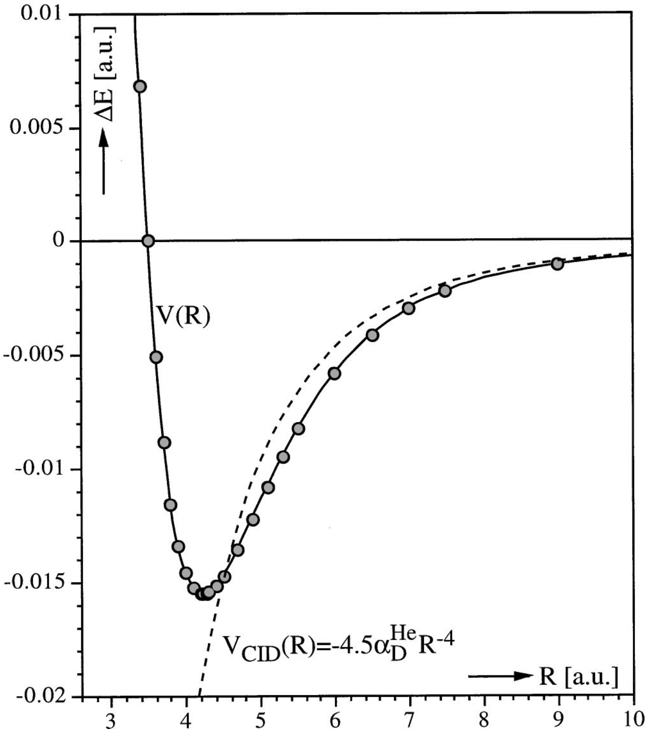

FIG. 1. Potential-energy curve of HeY^{3+}. The dots indicate the calculated DKCCSD(T) points, the solid line represents the extended Morse potential of Eq. (2), and the dashed curve the ion-induced dipole interaction.

that lighter HeX^{3+} species can be found that are stable, but they will be repulsive in the outer part of the potential-energy curve. The 0.42-eV dissociation energy of HeY^{3+} is slightly higher than the previously proposed rare-earth–helium HeX^{3+} dissociation energies D_e that lie between 0.20 and 0.39 eV [8]. The bonding situation can mainly be described by a charge-induced dipole (CID) interaction [18]

$$V_{\text{CID}}(R)=-\frac{q^2}{2}\alpha_D^{\text{He}}R^{-4}, \tag{1}$$

where q is the charge of the cation ($q=3$ for Y^{3+}), α_D^{He} is the static dipole polarizability of He (1.383 a.u.) [19], and R the internuclear bond distance. Y^{3+} as a small cation allows for a short equilibrium bond distance of 224 pm, thus rendering $V_{\text{CID}}(R_e)$ relatively large. A comparison of the $V_{\text{CID}}(R)$ curve with the calculated BO potential-energy curve $V(R)$ at the DKCCSD(T) level is given in Fig. 1. Both curves agree nicely for longer distances and start to significantly deviate at smaller distances than the equilibrium bond distance R_e where repulsive forces in the BO potential become non-negligible. Second, a charge-density Mulliken analysis also reveals that the system can mainly be described as a CID interaction, as the atomic charges are almost perfectly zero for He and +3 for Y at R_e. Third, note that the spectroscopic constants at the HF level are reasonably close to the correlated values (Table II), as small correlation effects can be expected for a classical CID interaction.

The plotted BO potential-energy curve (Fig. 1) represents an approximation of the DKCCSD(T) points by an extended Morse potential,

TABLE II. Spectroscopic constants for HeY$^+$. Hartree-Fock, HF, second-order many-body perturbation theory, MBPT2, and coupled cluster singles-doubles with noniterative triples, CCSD(T). Bond distances R_e in pm, bond dissociation energies, D_e and D_0 (the latter corrected for vibrational contributions) in eV, harmonic frequencies ω_e in cm^{-1}, first and second anharmonicity constant $\omega_e x_e$ and $\omega_e y_e$ in cm^{-1}, rotational constant B_e in cm^{-1}, centrifugal distortion constant C_e in 10^{-5} cm^{-1}, vibration-rotational coupling constant α_e in cm^{-1}. The sign convention of Huber and Herzberg is used [1].

	HF	MBPT2	CCSD(T)
R_e	230.0	223.7	224.3
D_e	0.336	0.413	0.421
D_0	0.312	0.387	0.394
ω_e	389	432	437
$\omega_e x_e$	16.8	15.6	15.8
$\omega_e y_e$	0.150	0.042	0.052
B_e	0.832	0.878	0.877
C_e	1.17	1.14	1.12
α_e	0.036	0.033	0.032

$V(R)=\sum_{i=1}^{n} A_i e^{-\alpha_i(R-R_e)}$ using the boundary condition

$$D_e=-\sum_{i=1}^{n} A_i, \tag{2}$$

where A_i and α_i are fit parameters. The original Morse potential is a special case of Eq. (2) with $n=2$, $A_2=D_e$, and $\alpha_2=2\alpha_1$, and gives a good description for short distances and the equilibrium while the deviation towards the dissociation becomes significant. Using our extended version, an excellent least-squares fit along the entire potential curve is obtained by the choice of $n=4$ and the following parameters (atomic units are used throughout): $A_1=+0.042\,33$, $A_2=-0.026\,16$, $A_3=+0.045\,49$, $A_4=-0.077\,12$, $\alpha_1=0.7727$, $\alpha_2=0.5518$, $\alpha_3=0.6279$, and $\alpha_4=0.1986$. The modeled potential-energy curve can accommodate up to 14 vibrational energy levels. The calculated vibrational-rotational constants listed in Table II will help to identify this gas phase species by future experimental work. We finally mention that the next transition element compound HeZr^{3+} may also be stable, as the experimental ionization potential $V_{\text{IP}_2}(\text{Zr}^{2+})=24.8$ eV only slightly exceeds $V_{\text{IP}_0}(\text{He})$ [5]. Furthermore, the recently published ionization potentials for the actinide series of elements makes in unlikely that a purely bound potential curve can be found for a quadruply charged species, XY^{4+} (the smallest fourth ionization potential in the lanthanide or actinide series is that of Th with 28.65 eV) [20].

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