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The characteristics of doubly and triply charged ions C_2^{2+}, C_2^{2-} and C_2^{3+}*

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Based on group theory and atomic and molecular reaction statics, this paper derives the possible electronic states of C_2^{2+}, C_2^{2-} and C_2^{3+}, and their reasonable dissociation limits and determines their ground electronic states $C_2^{2+}(X^3\Pi_u)$, $C_2^{2-}(X^1\Sigma_g^+)$ and $C_2^{3+}(X^4\Sigma_u^-)$ using quantum mechanical calculations at the level of QCISD/6-311G*. All the potential energy curves of their ground states have both a minimum and a maximum, which are the so-called "energy trapped" molecules. This sort of potential maximum is chiefly due to Coulomb repulsion. We propose the perturbation effect of ionic charges, which is used to explain why the orbital degeneracy of diatomic ions may be removed. The characteristics of potential curves for diatomic ions are briefly described.

Keywords: C_2 ions, electronic states, potential energy function
PACC: 3120, 3120D

1. Introduction

The diatomic ion is a current topic of interest that is not only of great practical importance, but also very valuable with regard to theoretical considerations. Most researchers have focused on the singly charged diatomic ions,[1−5] and some of them are interested in the doubly charged diatomic ions, for example, C_2^{2+}. There have been quite good works with C_2^{2+}. Hogreve[2] studied the structure and the potential energy curve of C_2^{2+}, which are similar to those of Bruna and Wright.[6] However, few papers have been concerned with C_2^{3+} and C_2^{2-}. Possibly, the ions that are greater than triply charged may always be unstable.

In comparison with the neutral diatomics, diatomic ions exhibit some new features. For example, the doubly charged ions AB^{2+} with the dissociation channel $A^+ + B^+$ always have a potential maximum except the minimum, then, this sort of potential energy curves is a trapped energy well shape called a "volcano".[7] This feature changes the character of the ground-state vibrational levels from discrete to quasi-discrete, since they are all embedded in the continuum. Therefore, it is necessary to explore the cause of the maximum formed. In addition, the doubly charged ions like AB^{2+} may have more competitive dissociation channels, such as $A^{2+}+B$, $A+B^{2+}$ or $A^+ + B^+$. So the problem is complicated.

One more problem is to examine the perturbation effect of ionic charges, for diatomic ions orbital degeneracy may or may not be removed. This kind of degeneracy is different from the Jahn–Teller or Renner–Teller effect, as there is no bending vibration.

For almost all neutral or singly charged diatomic molecules, the ground state has only one stationary point, namely the minimum. The extended Rydberg function, i.e. the Murrell–Sorbie function,[8−11] is the most satisfactory theoretical method for accurately describing the behaviour of these neutral or singly charged diatomic molecules in the equilibrium region.

However, the extended Rydberg function is unsatisfactory for doubly or triply charged diatomic ions. Zhu, Wang and co-workers[12−14] proposed an analytical potential energy function of doubly charged diatomic molecules, and it is used successfully to many doubly charged diatomic ions. In general, the potential energy curve of triply charged ions is repulsive. But the potential energy curve of C_2^{3+} is similar to that of doubly charged ions. Based on this point, we extend the analytical potential energy function for doubly charged ions and the triply charged ions. And we have obtained some good results. For the first time as far as we know, the potential energy function for

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doubly charged ions is applied to C_2^{2-} successfully.

Using the software Gaussian 98,[15] we study the characteristics of C_2^{2+}, C_2^{2-} and C_2^{3+} in detail.

2. Electronic states and dissociation limits

The optimum energy process for C_2^{2+} is the dissociation channel $C^+ + C^+$ with the ground state ^2P_u for both C^+. Based on the group theory and atomic and molecular reaction statics,[16,17] the representation ^2P_u of atomic group $O(3)$ is resolved into the direct sum $^2\Sigma_u^+ \oplus ^2\Pi_u$ of $D_{\infty h}$ for C_2^{2+}, and then the direct product $(^2\Sigma_u^+ \oplus ^2\Pi_u) \otimes (^2\Sigma_u^+ \oplus ^2\Pi_u)$ will give all the possible electronic states for C_2^{2+}, i.e. $^1\Sigma_g^+$ (2), $^1\Sigma_u^-$, $^1\Pi_g$, $^1\Pi_u$, $^1\Delta_g$, $^3\Sigma_u^+$ (2), $^3\Sigma_g^-$, $^3\Pi_g$, $^3\Pi_u$ and $^3\Delta_u$. In addition, the calculations for the triplet of C_2^{2+} at the level of QCISD/6-311G* described below give the electronic configuration as $\sigma_g^2\sigma_u^2\sigma_g^2\sigma_u^2\sigma_g\pi_u$ and the electronic state as $^3\Pi_u$, which is one of the possible electronic states shown above. The calculations with the same method show that the energy for triplet is lower than that of singlet by 7.62 eV. It is believed that the ground state of C_2^{2+} is $X^3\Pi_u$. One of the excited states calculated is $^3\Sigma_g^-$ for C_2^{2+}. According to the principle of microscopic reversibility, the correct dissociation limit must be

$$C_2^{2+}(X^3\Pi_u) \rightarrow 2C^+(^2P_u)$$

and

$$C_2^{2+}(^3\Sigma_g^-) \rightarrow 2C^+(^2P_u).$$

They will be used to represent the potential energy curves.

For C_2^{2-} ion, the optimum energy dissociation channel is $C^- + C^-$ with the ground state ^4S_u for both C^-. The same method of resolution and direct product of group representations shows that $^4\Sigma_u^- \otimes {}^4\Sigma_u^- = {}^1\Sigma_g^+ \oplus {}^3\Sigma_u^+ \oplus {}^5\Sigma^+ \oplus {}^7\Sigma_u^+$, and there are 4 possible symmetric states. The singlet $^1\Sigma_g^+$ is the ground state of C_2^{2-} by the calculations, i.e. $C_2^{2-}(X^1\Sigma_g^+)$, its dissociation limit is

$$C_2^{2-}(X^1\Sigma_g^+) \rightarrow 2C^-(^4S_u).$$

The optimum energy dissociation channel for C_2^{3+} is $C^{2+} + C^+$, where the ground state and the first excited state[18] for C^+ are ^2P_u and ^4P_g with an energy interval 43000.2cm^{-1}, and the ground state and the first excited state[18] for C^{2+} are ^1S_g and ^3P_u with an energy interval 52315.0cm^{-1}. If both C^+ and C^{2+} are in their ground states, i.e., $C^+(^2P_u)+C^{2+}(^1S_g)$, C_2^{3+} would be a doublet. Otherwise, if one of them is in ground state, the other is in the first excited state, there will be two possible combinations, i.e., $C^{2+}(^1S_g)+C^+(^4P_g)$ and $C^{2+}(^3P_u)+C^+(^2P_u)$. The energy interval for C^{2+} is larger than that of C^+, so, the favourable combination would be $C^{2+}(^1S_g)+C^+(^4P_g)$. Based on the resolution and direct product of group representations and in consideration of the exchange of ionization potential of the identical carbon atom, the optimum combination $C^{2+}(^1S_g)+C^+(^4P_g)$ will result in all the possible electronic states $^4\Sigma_g^-$, $^4\Sigma_u^-$, $^4\Pi_g$ and $^4\Pi_u$ for C_2^{3+} ion. The other combination $C^{2+}(^3P_u)+C^+(^2P_u)$ will result in all the possible electronic states $^{2,4}\Sigma_g^+(2)$, $^{2,4}\Sigma_u^+(2)$ $^{2,4}\Sigma_g^-$, $^{2,4}\Sigma_u^-$, $^{2,4}\Pi_g(2)$, $^{2,4}\Pi_u(2)$, $^{2,4}\Delta_g$, and $^{2,4}\Delta_u$, for C_2^{3+} ion. The calculations show that the combination $C^{2+}(^1S_g)+C^+(^4P_g)$ gives the lowest state $^4\Sigma_u^-$ with an energy −73.210 95 a.u., and the combination $C^{2+}(^3P_u)+C^+(^2P_u)$ gives the lowest state $^2\Pi_u$ with an energy −73.025 30 a.u. The energy difference between $^4\Sigma_u^-$ and $^2\Pi_u$ is 0.1857 a.u. or 5.05 eV. So, we come to the conclusion that the ground state for C_2^{3+} is $X^4\Sigma_u^-$, which is in agreement with the calculated results, i.e. electron configuration $\sigma_g^2\sigma_u^2\sigma_g^2\sigma_u\pi_u^2$ and electronic state $^4\Sigma_u^-$. The dissociation limit is

$$C_2^{3+}(X^4\Sigma_u^-) \rightarrow C^{2+}(^1S_g) + C^+(^4P_g).$$

3. Potential energy function form

Zhu in Refs. [12]–[14] has proposed a new analytical potential energy function with four parameters (Wang added the extra parameter a_4) to describe the diatomic ions with both potential minimum and maximum or without any stationary point. The function form proposed is

$$E = \frac{a_1}{\rho - a_2} - \frac{a_3}{(\rho + a_4)^2}, \tag{1}$$

where $\rho = R - R_{\min}$ is the displacement from minimum for diatomic ions with both potential minimum and maximum, and $\rho = R$ only for the repulsive states. Equation (1) can be rewritten in a typically cubic form of ρ

$$\rho^3 + \rho^2\left(2a_4 - a_2 - \frac{a_1}{E}\right) + \rho\left(a_4^2 - 2a_2a_4 + \frac{a_3}{E} - \frac{2a_1a_4}{E}\right) - \left(a_2a_4^2 + \frac{a_2a_3}{E} + \frac{a_1a_4^2}{E}\right) = 0. \tag{2}$$

If the potential energy E lies between the maximum and minimum, i.e. $E_{\min} < E < E_{\max}$ (see the figures) there will be three real roots; if $E > E_{\max}$ or $E < E_{\min}$, there will be one real root and a pair of imaginary roots. Equations (1) and (2) are in a mathematically reasonable form, a_1-a_4 are the characteristic parameters of a particular molecule.

Based on the first derivatives at minimum and maximum, it is easy to obtain the following relations:

$$\frac{a_1}{a_2^2} = \frac{2a_3}{a_4^3}, \tag{3}$$

where $\rho = R - R_{\min}$=0, and

$$\frac{a_1}{(\rho - a_2)^2} = \frac{2a_3}{(\rho + a_4)^3}, \tag{4}$$

where $\rho = R_{\max} - R_{\min}$. The quadratic, cubic, and quartic force constants have been derived from Eq.(1) at the minimum, which is regarded as the equilibrium state.

$$f_2 = \frac{2a_1}{(-a_2)^3} - \frac{6a_3}{a_4^4}, \tag{5}$$

$$f_3 = -\frac{6a_1}{(-a_2)^4} + \frac{24a_3}{a_4^5}, \tag{6}$$

$$f_4 = \frac{24a_1}{(-a_2)^5} - \frac{120a_3}{a_4^6}. \tag{7}$$

The expressions relating the force constants f_i with spectroscopic constants for diatomic molecules could be expressed as

$$f_2 = 4\pi^2\mu\omega_e^2c^2, \tag{8}$$

$$f_3 = -\frac{3\left(1 + \dfrac{\alpha_e\omega_e}{6B_e^2}\right)f_2}{R_{\min}}, \tag{9}$$

$$f_4 = \frac{\left[15\left(1 + \dfrac{\alpha_e\omega_e}{6B_e^2}\right)^2 - \dfrac{8\omega_e\chi_e}{B_e}\right]f_2}{R_{\min}^2}, \tag{10}$$

$$B_e = \frac{h}{8\pi^2c\mu R_e^2} = \frac{h}{8\pi^2cI_e}, \tag{11}$$

where ω_e, $\omega_e\chi_e$, B_e, α_e are the spectroscopic constants; c is the velocity of light, μ is the reduced mass for individual atoms.

4. Calculation and results

The molecular structures of $C_2^{2+}(X^3\Pi_u,\ ^3\Sigma_g^-)$, $C_2^{2-}(X^1\Sigma_g^+)$ and $C_2^{3+}(X^4\Sigma_u^-)$ have been optimized with *ab initio* QCISD/6-311G* method. First, in order to determine the ground states of C_2^{2+}, C_2^{2-}, C_2^{3+}, we optimized the structures of them based on the different possible multiplicities. The results are listed in Table 1, from which we can obtain the ground states of C_2^{2+}, C_2^{2-}, C_2^{3+}. They are $X^3\Pi_u$, $X^1\Sigma_g^+$, $X^4\Sigma_u^-$, respectively. As for C_2^{2+}, the nuclear distances are 0.17780 nm and 0.13099 nm at the minima and the energies are –2027.5978 and –2023.8566 eV, respectively, corresponding to the two electronic states with the same multiplicity 3. The nuclear distances of $C_2^{3+}(X^4\Sigma_u^-)$ and $C_2^{2-}(X^1\Sigma_g^+)$ are 0.15316 nm and 0.12864 nm and the energies are –1992.1944 and –2057.0797 eV at the minima, respectively. The harmonic frequencies of $C_2^{2+}(X^3\Pi_u)$, $C_2^{2+}(^3\Sigma_g^-)$, $C_2^{3+}(X^4\Sigma_u^-)$ and $C_2^{2-}(X^1\Sigma_g^+)$ are 535.7792, 1639.2154, 906.9496 and 1772.5027cm^{-1}, respectively.

Table 1. Energies of possible states of C_2^{2+}, C_2^{2-}, C_2^{3+}.

Molecule	Multiplicity	Electronic state	Energy/eV
	1	$^1\Sigma_g^+$	–2019.9829
C_2^{2+}	3	$^3\Pi_u$	–2027.5978
	3	$^3\Sigma_g^-$	–2023.8566
C_2^{2-}	1	$^1\Sigma_g^+$	–2057.0782
	3	–	–2051.9464
C_2^{3+}	2	–	–1987.1425
	4	$^4\Sigma_u^-$	–1992.1944

The potential energy curves for C_2^{2+}, C_2^{2-} and C_2^{3+} are calculated with the QCISD/6-311G* method, see Figs.1–4. With the nonlinear fitting method, we have obtained the parameters in Eq.(1) for C_2^{2+}, C_2^{2-} and C_2^{3+}, see Table 2. In Figs.1–4, the black squares represent the *ab initio* values and the solid lines denote the fitted curves. These figures show that the potential energy values from Eq.(1) proposed by Zhu and Wang are in good agreement with those from *ab initio* calculation, which demonstrates that this ZW Eq.(1) is a good formula to represent the potential energy function of doubly charged diatomic ions. It can also express the potential energy function for triply charged ion C_2^{3+} and doubly negative charged ion C_2^{2-} with both potential minimum and maximum. It is for the first time to apply Eq.(1) to a triply charged ion and a doubly negative charged ion with both potential minimum and maximum. The obtained results are satisfactory. The nuclear distances at the minimum and maximum and the energy difference between them are listed in Table 3.

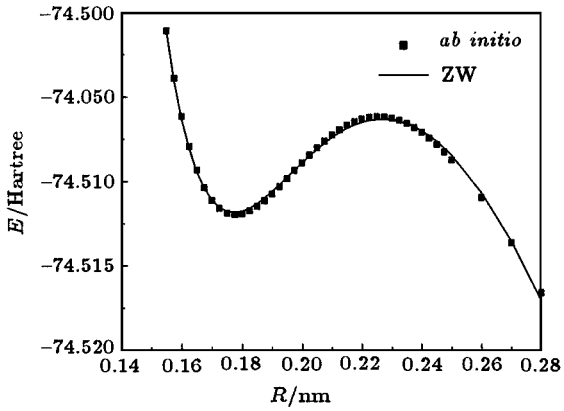


Fig.1. Potential energy curve of C_2^{2+} ($X^3\Pi_u$).

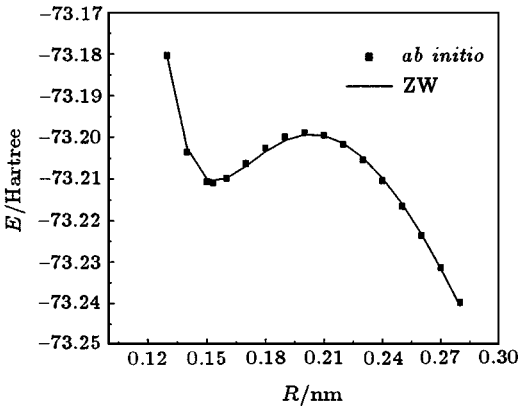


Fig.3. Potential energy curve of C_2^{3+} ($X^4\Sigma_u^-$).

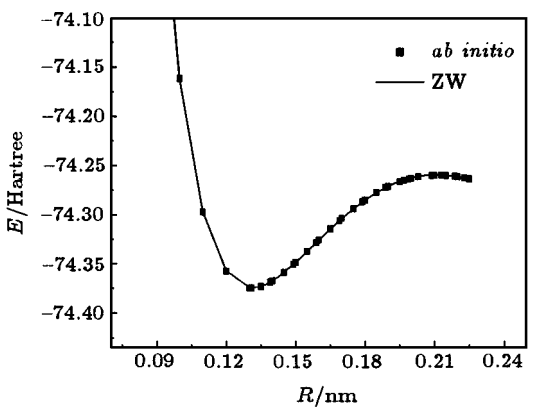


Fig.2. Potential energy curve of C_2^{2+} ($^3\Sigma_g^-$).

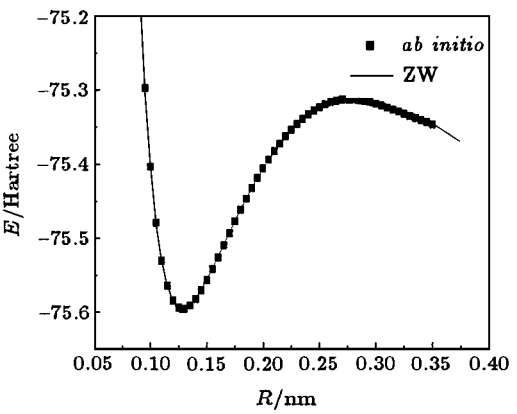


Fig.4. Potential energy curve of C_2^{2-} ($X^1\Sigma_g^+$).

Table 2. Parameters of the analytical potential energy function.

Molecule	R_{min}/nm	a_1/eV·nm	a_2/nm	a_3/eV·nm^2	a_4/nm
$C_2^{2+}(X^3\Pi_u)$	0.17780	9.8477	–0.12216	2.4129	0.19406
$C_2^{2+}(^3\Sigma_g^-)$	0.13099	122.63	–0.14571	38.015	0.23613
$C_2^{3+}(X^4\Sigma_u^-)$	0.15316	20.668	–0.12121	5.1041	0.19369
$C_2^{2-}(X^1\Sigma_g^+)$	0.12864	43.797	–0.12223	14.275	0.21352

Table 3. Calculated minimum and maximum for C_2^{2+}, C_2^{3+} and C_2^{2-}.

Molecule	$C_2^{2+}(X^3\Pi_u)$	$C_2^{2+}(^3\Sigma_g^-)$	$C_2^{3+}(X^4\Sigma_u^-)$	$C_2^{2-}(X^1\Sigma_g^+)$
R_{min}/nm	0.17780	0.13099	0.15316	0.12864
R_{max}/nm	0.22654	0.21065	0.20371	0.28475
ΔE=E_{max} − E_{min}/eV	0.1546	3.0731	0.3161	7.6865

From parameters a_1 – a_4, the force constants f_i (i=2,3,4) can be easily acquired by using Eqs.(5)–(7), and the spectroscopic constants ω_e, $\omega_e x_e$, B_e, α_e can be calculated by using Eqs.(8)–(11). The results are listed in Table 4. From the table, we can see that the equilibrium nuclear distance for C_2^{2+} is in fairly good agreement with that given in Refs. [2] and [6].

Table 4. Derived force constants and spectroscopic data.

Molecule	R_{min}/nm	ω_e/cm^{-1}	$\omega_e\ x_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	f_2/aJ·nm^{-2}	f_3/aJ·nm^{-3}	f_4/aJ·nm^{-4}
$C_2^{3+}(X^4\Sigma_u^-)$	0.15316	906.950	25.31805	1.1881	0.03165	233.388	–20067.6	1179630
$C_2^{2-}(X^1\Sigma_g^+)$	0.12864	1772.503	10.32805	1.6841	0.01508	1083.72	–64926.8	3277290
$C_2^{2+}(X^3\Pi_u)$	0.17780	535.779	30.34029	0.8816	0.03891	95.2307	–8790.79	523077
$C_2^{2+}(^3\Sigma_g^-)$	0.13099	1639.215	14.32366	1.6242	0.01814	946.100	–62366.2	2961850
$C_2^{2+}(X^3\Pi_u)$[2]	0.16933	–	–	–	–	–	–	–
$C_2^{2+}(X^3\Pi_u)$[6]	0.1728,0.1705		–	–	–	–	–	–

The present method for expressing the analytical potential function is not only reasonable to either one or three different interatomic distances for a given potential energy, but also quite flexible for application. If one has derived a potential curve by *ab initio* calculations, it is easy to obtain the parameters $a_1 - a_4$ by a least-squares fitting, then derive f_2, f_3 and f_4 from Eqs.(4)–(6) and the spectroscopic constants from Eqs.(7)–(10). This is based on the first principle. The inversion problem is also straightforward. One of the main objectives in giving this account of doubly charged diatomic ions is to prepare the ground for a description of potential for polyatomic ions, which is under investigation. We apply the ZW equation to the doubly negative charged ion C_2^{2-} and obtain a satisfactory result.

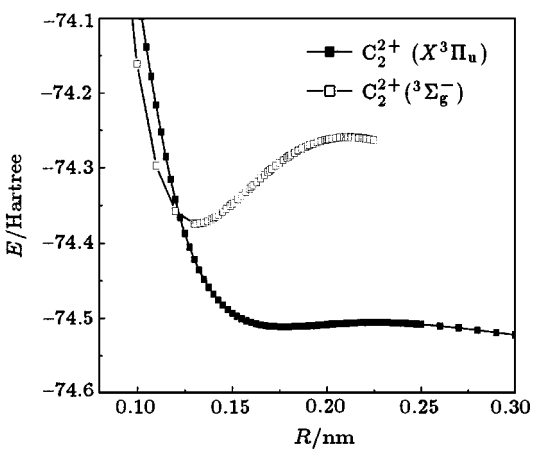


Fig.5. Potential energy curve of C_2^{2+}.

In this paper, we encounter the same problem as C^{2+}[19] in the case of determining the ground state of C_2^{2+}. There is an intercross of two potential energy curves of C_2^{2+} (see Fig.5), for the state $X^3\Pi_u$ and $^3\Sigma_g^-$ of C_2^{2+} are different irreducible representations of group $D_{\infty h}$. If one optimizes the equilibrium nuclear distance from the left-hand side, i.e., $R_{initial} < R_e$, the first minimum will be the state $^3\Sigma_g^-$, whereas, if the optimization starting from the right-hand side, i.e., $R_{initial} > R_e$, then it will be the state $X^3\Pi_u$. This situation may be rather frequent, so, it should be careful to deal with the problem. When determining the ground state of a diatomic molecule, we should start optimization from both sides of the equilibrium.

5. Discussion and summary

5.1. The potential maximum due to Coulomb repulsion

It is well known that there are three different types of potential maxima for diatomic molecules or ions, i.e., the potential maximum results from predissociation, or van der Waals interaction, or the noncrossing of potential curves of two states with the same irreducible representation for a given molecular group.[16,20] The fourth is due to Coulomb repulsion between an atomic ion pair with the same charges.[14,20] The Coulomb repulsive potential is closely related to the interionic distance and proportional to the product of ionic charges; therefore, the highly charged molecular ions would always be unstable.

From this paper, we believe that the fourth potential maximum can be explained by orbital symmetry, and it is in a position to affirm this sort of potential maximum. For diatomics or its ions, the energy level relations between the separated atoms on the one hand, i.e., the dissociation limit of diatomics, and the united atom on the other hand, are the so-called correlation rules, which include those in which the symmetry of each molecular orbital (MO) remains unchanged, the MOs with the same symmetry, i.e., the same irreducible representation cannot cross, and all the atomic orbital (AO) and MOs are conservative during the process from the separated atoms to the united atom, for MOs are formed based on the resolution and direct product of AOs as the group representation of an atomic group.[21]

The general potential curves with only one mini-

mum for diatomics satisfy all the conditions described above, that is, it is allowed by orbital symmetry. However, the potential curves with both minimum and maximum will not satisfy all those conditions, for there are no MOs formed starting from the separated atoms until to the maximum (see Fig.1, the potential energy curve of $C_2^{2+}(X^3\Pi_u)$), that is, it is forbidden by orbital symmetry. In fact, this sort of maximum exists indeed. From the separated atoms to the maximum, there is mainly ionic bond, therefore, the potential rises as the Coulomb repulsion increases with decreasing interatomic distance; on the contrary, if MOs were formed, the potential should not rise but fall gradually. Therefore, the fourth potential maximum is chiefly due to the Coulomb repulsion.

5.2.The perturbation effect of ionic charges

There is a general theorem called the Jahn–Teller effect,[22−24] which states that if nonlinear molecules are in an orbitally degenerate state, the system will distort so as to reduce the symmetry and remove the degeneracy due to the interaction of vibrational and electronic motions. Even for linear molecules the so-called Renner–Teller effect[25] may remove the degeneracy.

For diatomics, there is no any bending vibration; however, the perturbation effect of ionic charges may also remove the degeneracy. The energy of a perturbed system can be expressed as

$$E = E^0 + \langle\psi^0|\hat{H}'|\psi^0\rangle + \sum_{n\neq 0} \frac{|\langle\psi^0|\hat{H}'|\psi^n\rangle|^2}{E^0 - E^n} + \cdots, \quad (12)$$

where there are the zero-order, first-order and second-order perturbation energies, etc. The perturbation operator is

$$\hat{H}' = \frac{q_1 q_2}{R}, \quad (13)$$

where R is the nuclear distance, and q_1 and q_2 are the electric charges for dissociated ions. The state wavefunction may be either degenerate or non-degenerate. If it is non-degenerate, the first-order perturbation $\langle\psi^0|\hat{H}'|\psi^0\rangle$ over all space can only be non-zero with a positive value, because H' for diatomic ions is always symmetric and the integrand is totally symmetric. If it is degenerate, for example, in doubly orbitally degenerate states, such as, in Π, Δ and Φ states, etc., its direct product with itself must contain an antisymmetric part which causes this part of contribution to be zero, not positive value. Therefore, in comparison with that of non-degenerate, the energy level for diatomic ions will descend, and the degeneracy will be removed.

As for the second-order perturbation, i.e., the third term of Eq.(12), it is always negative, for $E_0 - E_n < 0$. However, the excited states ψ^n must be of the same symmetry, i.e. the same irreducible representation with ψ^0; otherwise, the integrations will be zero, that is, there is no contribution from the second-order perturbation. If ψ^0 is degenerate, there is no contribution from either antisymmetric part or symmetric part, depending on whether ψ^n is symmetric or antisymmetric. Therefore, compared with that of non-degenerate, the energy level will ascend relatively. In the end, there are two opposite factors acting on the degenerate state ψ^0, one is from the first-order perturbation, and the other is from the second-order perturbation.

In summary, we come to the following conclusions. (a) The larger the ionic charges, the more unstable the molecular ions, so, the charges of molecular ions are not too large, like the atomic ions. (b) The molecular ions may be orbitally degenerate, such as, $C^{2+}(^4\Pi_u)$ and $C_2^{2+}(X^3\Pi_u)$, or may not be orbitally degenerate, such as, $C_2^{3+}(X^4\Sigma_u^-)$. This is due to the perturbation effect of $\hat{H}'$.

5.3.The characteristics of potential curves for diatomic ions

The singly charged diatomic ions have no potential maximum due to the Coulomb repulsion, for q_1 or q_2 must be zero, and then the perturbation operator $\hat{H}'$ vanishes. The doubly and triply charged diatomic ions usually have a potential maximum due to the Coulomb repulsion, which is forbidden by orbital symmetry described above. However, the potential maximum is certainly possible, for neither of q_1 and q_2 is zero from the dissociation limits of the ions C_2^{2+}, C_2^{2-} and C_2^{3+}, and their $\hat{H}'$ does not vanish, hence this maximum can be formed.

The series of studies[26,27] indicate that the ions $PuO^{2+}(X^5\Sigma^-)$, $PuH^{2+}(X^8\Sigma^-)$, $PuN^{2+}(X^4\Sigma^+)$ and $PuC^{2+}(X^9\Sigma^-)$ have no potential maximum, for the dissociation channel is $PuX^{2+} \rightarrow Pu^{2+} + X$ (X=H, N, O and C), the charge for one of them is zero. It is known that the second ionization potential of Pu is even less than the first ionization potential of H, N, O and C. In this case, there will be no perturbation effect of ionic charges.

As described above, the potential curves for either ions with both minimum and maximum or repulsive states can be represented by the typically cubic Eqs. (1) and (2), which are the mathematically reasonable form.

References

[1] Maier J P and Rösslein M 1988 *J. Chem. Phys.* **88** 4614
[2] Hogreve H 1995 *J. Chem. Phys.* **102** 3281
[3] Rosmus P, Werner H J, Reinsch E A and Larsson M 1986 *J. Electron. Spectrosc. Relat. Phenom.* **41** 289
[4] Kraemer W P and Roos B O 1987 *Chem. Phys.* **118** 345
[5] Petrongolo C, Bruna P J, Peyerimhoff S D and Buenker R J 1981 *J. Chem. Phys.* **74** 4594
[6] Bruna P J and Wright J S 1991 *J. Mol. Struct.* (Theochem) **230** 213
[7] Nicolaides C A, Mercouris T and Petsalakis I D 1993 *Chem. Phys. Lett.* **212** 685
[8] Murrell J N and Sorbie K S 1974 *J. Chem. Soc. Faraday Trans.* ii **70** 1552
[9] Murrell J N, Carter S, Frantos S C, Huxley P and Varandas A J C 1984 *Molecular Potential Energy Functions* (New York: Wiley)
[10] Huxley P and Murrell J N 1983 *J. Chem. Soc. Faraday Trans.* ii **79** 323
[11] Zhu Z H, Shen S Y, Mou W M and Li L 1984 *J. Molec. Sci.* **2** 79
[12] Zhu Z H *et al* 1997 *Mol. Phys.* **92** 1061
[13] Wang F H *et al* 1998 *Chin. Phys. Lett.* **15** 715
[14] Wang F H *et al* 1998 *J. Mol. Struct.* (Theochem) **453** 71
[15] Frisch M J 1998 GAUSSIAN 98 REVISION
[16] Zhu Z H 1996 *Atomic and Molecular Reaction Statics* (Beijing: Science Press) (in Chinese)
[17] Herzberg G 1966 *Molecular Spectra and Molecular Structure*, vol. 1, *Spectra of Diatomic Molecules* (Princeton, NJ: Van Nostrand company)
[18] Moore C E 1949 *Atomic Energy Levels* (National Bureau of Standards, Circ. 467)
[19] Wang R and Zhu Z H 2001 *J. Molec. Struct.* (Theochem) **571** 133
[20] Zhu Z H and Yu H G 1997 *Molecular Structure and Molecular Potential Energy Function* (Beijing: Science Press)
[21] Ludwig W and Falter C 1995 *Symmetries in Physics* (Berlin: Springer-Verlag)
[22] Jahn H A and Teller E 1937 *Proc. R. Soc.* A **161** 220
[23] Öpik U and Pryce M H L 1937 *Proc. R. Soc.* A **238** 425
[24] Wang R, Zhu Z H and Yang C L 2001 *Acta Phys. Sin.* **50** 1675 (in Chinese)
[25] Renner R 1934 *Z. Phys.* **92** 172
[26] Li Q, Liu X Y, Gao T and Zhu Z H 2000 *Acta Physico-Chimica Sinica* **16** 987
[27] Li Q, Liu X Y, Wang H Y and Zhu Z H 2000 *Acta Phys. Sin.* **49** 2347 (in Chinese)