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Accurate ab initio calculation of potential energy curves and transition dipole moments of the Xe_2^+ molecular ion

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Abstract

A complete set of accurate ab initio data is produced for the low-lying electronic states of Xe_2^+ , including potential energy curves and transition dipole moments, using a coupled cluster approach (RHF-RCCSD-T), accurate relativistic effective core potentials and an extended basis set. This set of data can be useful for spectroscopical studies as well as for modeling of the dynamics of Xe_n^+ clusters. The spin–orbit coupling is included through a semiempirical treatment. The spectroscopic constants for Xe_2^+ are in very good agreement with the experimental results. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Despite considerable experimental and theoretical interests, potential energy curves of rare gas dimer ions are not known as precisely as could be expected for diatomic molecular ions of such an importance. Experimentally, even the most fundamental spectroscopic constants, such as the binding energy of the ground state, were controversial for a long time [1–3]. Only recently, they have been measured accurately for argon [2,3], xenon [4,5] and krypton [1]. The main difficulty in the experiment arises from the rather different

equilibrium distance of the ionic and the neutral dimer, from which the ions are produced. This difference leads to vanishing Franck–Condon factors for the excitation towards the lowest vibrational levels of the dimer ion. Concerning the theory, pioneering results were given by Wadt using the POLCI techniques [6,7]. However, accurate results are rather difficult to obtain, because of a large number of electrons involved and the necessity to treat, in a balanced way, various electronic effects (localization–delocalization of charge, static and dynamical polarization, resonant interactions, etc.).

Qualitatively, rare gas dimer ions are striking examples for an application of a simple mono-electronic picture. For the close shell neutral dimer, all bonding and antibonding orbitals are filled with two electrons and the resulting over-all

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interaction is rather repulsive. An alternative description could be no interaction between the two closed shell atoms. Removing an electron from an antibonding orbital leads to stabilization of the corresponding state and to a well on the potential curve, while removing an electron from a bonding orbital leads to repulsive curves. On the other hand, a no-interaction description of neutral dimer predicts flat curves for the ion, too. About the equilibrium geometry the dimer ion is characterized by a set of four curves, with a strong stabilization for the lowest Σ_u state, small attractive and repulsive character for the higher lying Π_g and Π_u states, and finally a strongly repulsive character for the highest Σ_g state, thus discarding a non-interacting scheme. This qualitative behavior is consistent with the mono-electronic approach, and allows for a basic understanding of the attractive and repulsive character of the various curves of the ion. However, accurate calculations represent a real challenge. Also, spin–orbit interactions should be taken into consideration, in particular for the heavier dimers. For the inner atomic shells they are usually treated implicitly by use of relativistic pseudopotentials, for the valence electrons they have to be treated explicitly.

Ionic rare gas clusters have attracted large attention from experimentalists as well as from theoreticians. They can be easily produced, mass selected, excited, and analyzed. Their fragmentation dynamics makes it possible to study interesting and fundamental process such as the competition between evaporation and fission which arises from the excess energy redistribution. Diatomic in molecules (DIM) approaches have been developed to enable studying the dynamics [8–12]; their essential input is the set of curves of the ionic dimer. In the DIM methods, effective interactions are extracted from the dimer and they are assumed to be transferable to the larger system. The quality of the diatomic inputs is an important criterion for the validity of the DIM models. In our previous study, we performed *ab initio* calculations for Ar_2^+ and He_2^+ [9]. We follow a similar objective in the present work concerning to Xe_2^+ , taking benefit of the recent improvements in the relativistic pseudopotential necessary for the *ab initio* treatment of this heavy atom [13].

The aim of this paper is to provide a reliable complete set of *ab initio* data including low-lying potential energy curves and transition dipole moments, useful for spectroscopical studies and for modeling of larger Xe_n^+ clusters and their dynamics.

2. Computation

2.1. *Ab initio* calculations

The RHF-RCCSD-T [14,15] method and the program package MOLPRO [16] were used for the calculation of the four lowest electronic states of the Xe_2^+ ionic dimer, $^2\Sigma_g^+$, $^2\Sigma_u^-$, $^2\Pi_g$, and $^2\Pi_u$. The inner shell electrons have been treated by using relativistic effective core potentials developed for rare-gas atoms by Nicklass et al. [13], the core polarization potential was included into the calculation.

The valence basis set used in the present calculation is essentially the basis set of Ref. [13] optimized for atomic dipole and quadrupole polarizabilities of Xe atom (8s8p6d6f)/[6s6p6d6f]. In order to get accurate interaction energies we have augmented this basis set by two g orbitals. Their exponents were optimized in order to yield, in the CI calculation, the maximum correlation energies of the ground state of Xe_2^+ both at the equilibrium and at asymptotic nuclear separations. Fig. 1 shows that the maximum correlation energies at both geometries correspond to the values $g_1 = 0.8$ and $g_2 = 0.375$. This choice consequently insures minimal correlation energy basis set superposition error. As can be seen in Fig. 1, exponents not optimal for both geometries may lead to unbalanced treatments for the correlation energy and therefore to artificially larger or smaller binding energies. Further trials to extend the basis set (three g orbitals) did not yield any significant changes of interaction energies and the (8s8p6d6f2g)/[6s6p6d6f2g] basis set was used throughout the calculation. The use of this basis set is sustained by the good agreement of the calculated (CCSD-T) values of xenon ionization potential $\text{IP} = 12.46$ eV, xenon dipole polarizability $\alpha = 26.88a_0^3$ and the $^2\text{P} \rightarrow ^2\text{S}$ excitation energy of the Xe^+ ion $\text{EX} = 10.98$ eV with the

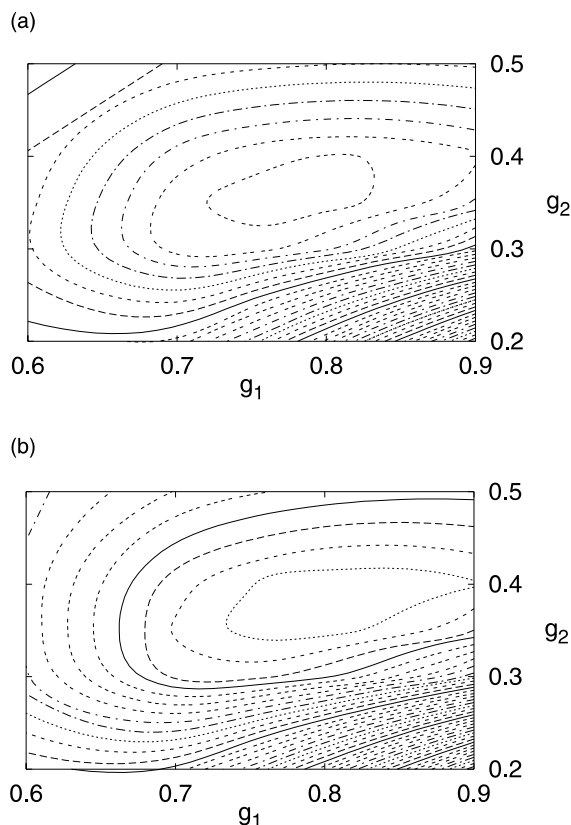


Fig. 1. Optimization of the exponents of the two g orbitals at (a) equilibrium and (b) asymptotic nuclear separations.

experimental spin-orbit averaged values: IP = 12.565 eV, EX = 10.832 eV, and $\alpha = 27.815a_0^3$ [17].

The splitting of the 2P ground state of Xe^+ by spin-orbit coupling into $^2P_{3/2}$ and $^2P_{1/2}$ states is 1.31 eV and cannot be neglected in the calculation of the potential curves of the Xe_2^+ ionic dimer. The spin-orbit interaction splits the four electronic states $^2\Sigma_g^+$, $^2\Sigma_u^+$, $^2\Pi_g$, and $^2\Pi_u$ into six states $I(1/2)_u$, $I(3/2)_g$, $I(3/2)_u$, $I(1/2)_g$, $II(1/2)_u$, and $II(1/2)_g$. The simple but effective treatment of the spin-orbit interaction given by the Cohen and Schneider semiempirical atom-in-molecule scheme [18] has been used in the present calculation. Previous studies (e.g. Refs. [6,7,9]), have demonstrated the reliability of this approach for the whole Rg_2^+ series.

RHF-RCCSD-T calculations were performed for internuclear distances from $R = 4.25$ to 15 au. For larger R , the use of the single reference RHF-

RCCSD-T method is not justified, but the potentials can be extrapolated analytically with the usual expression

$$E(R) = -\alpha/2R^4 + E_\infty \quad (1)$$

that characterizes the asymptotical behavior of all the considered potential energy curves. The smooth pass from the ab initio parts of curves to the analytical expression Eq. (1) can be assured by cubic spline fits and by the use in Eq. (1) of the constants that are compatible with the present calculation. Namely, the asymptotic energy E_∞ determined as a sum of the RCCSD-T energies of Xe and Xe^+ , $E_\infty = -30.764183$ au, and the experimental value of the dipole polarizability of xenon $\alpha = 27.815$ cm³ [17].

The RHF-RCCSD-T potential energy curves of the electronic states $^2\Sigma_g^+$, $^2\Sigma_u^+$, $^2\Pi_g$, and $^2\Pi_u$ are presented in Fig. 2 and in Table 1, the transition dipole moments among these states are plotted in Fig. 3. As expected from the point charge model, the main transition moments for the u-g transitions

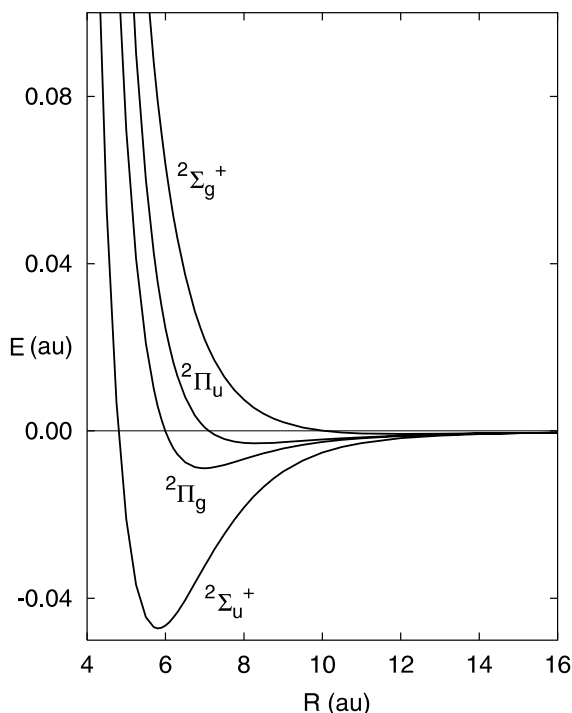


Fig. 2. Potential energy curves for Xe_2^+ without spin-orbit coupling.

Table 1
Energies for the four states of Xe_2^+ without SO in au

R	$^2\Sigma_u^+$	$^2\Sigma_g^+$	$^2\Pi_u$	$^2\Pi_g$
4.250	–30.637964	–30.326897	–30.360405	–30.480118
4.500	–30.711075	–30.430750	–30.482186	–30.578568
4.750	–30.757167	–30.511894	–30.568992	–30.646186
5.000	–30.785030	–30.573386	–30.630426	–30.692067
5.250	–30.800730	–30.619524	–30.673635	–30.722758
5.500	–30.808456	–30.654238	–30.703865	–30.742957
5.700	–30.810847	–30.675769	–30.721277	–30.753817
5.800	–30.811147	–30.684856	–30.728236	–30.757918
5.900	–30.810989	–30.692983	–30.734226	–30.761299
6.000	–30.810457	–30.700253	–30.739372	–30.764064
6.100	–30.809622	–30.706759	–30.743785	–30.766303
6.200	–30.808547	–30.712582	–30.747561	–30.768095
6.300	–30.807286	–30.717797	–30.750784	–30.769508
6.500	–30.804375	–30.726657	–30.755859	–30.771426
6.750	–30.800351	–30.735340	–30.760231	–30.772587
6.900	–30.797877	–30.739536	–30.762077	–30.772833
7.000	–30.796240	–30.741985	–30.763058	–30.772863
7.100	–30.794626	–30.744190	–30.763873	–30.772811
7.250	–30.792271	–30.747094	–30.764834	–30.772613
7.500	–30.788578	–30.751041	–30.765904	–30.772074
7.750	–30.785225	–30.754104	–30.766504	–30.771396
8.000	–30.782236	–30.756491	–30.766797	–30.770675
8.250	–30.779609	–30.758356	–30.766894	–30.769966
8.500	–30.777324	–30.759816	–30.766868	–30.769301
8.750	–30.775354	–30.760960	–30.766769	–30.768694
9.000	–30.773668	–30.761857	–30.766628	–30.768152
9.500	–30.771014	–30.763105	–30.766302	–30.767254
10.000	–30.769119	–30.763859	–30.765982	–30.766576
10.500	–30.767776	–30.764298	–30.765697	–30.766067
11.000	–30.766823	–30.764535	–30.765451	–30.765681
12.000	–30.765654	–30.764677	–30.765058	–30.765147
13.000	–30.765038	–30.764628	–30.764781	–30.764815
14.000	–30.764700	–30.764529	–30.764590	–30.764602
15.000	–30.764501	–30.764430	–30.764455	–30.764459

in either Σ or Π symmetries behaves as $R/2$. There are, however, some deviations particularly at shorter distances which could lead to noticeable effects for the absorption spectra of Xe_n^+ clusters [10,19]. The six electronic states arising from the inclusion of the spin–orbit coupling through the Cohen and Schneider scheme [18] are represented in Fig. 4 and Table 2, the corresponding transition dipole moments are plotted in Fig. 5. The complete set of numerical data is available on request.

2.2. Spectroscopical constants

A check of the quality of ab initio potential energy curves can be done by comparison of the

computed spectroscopical constants with the available data from high resolution threshold photoelectron spectroscopy experiments [4,5].

For the six spin–orbit electronic states of Xe_2^+ , the vibrational levels were calculated by numerical integration of the Schrödinger equation by use of the Cooley–Numerov technique [20,21] and cubic spline of the potential energy curves. The calculations were done for the $^{131.3}\text{Xe}_2^+$ isotopic species. The least square fits of the vibrational energies

$$G(v) = T_e + \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \omega_e y_e(v + 1/2)^3 \quad (2)$$

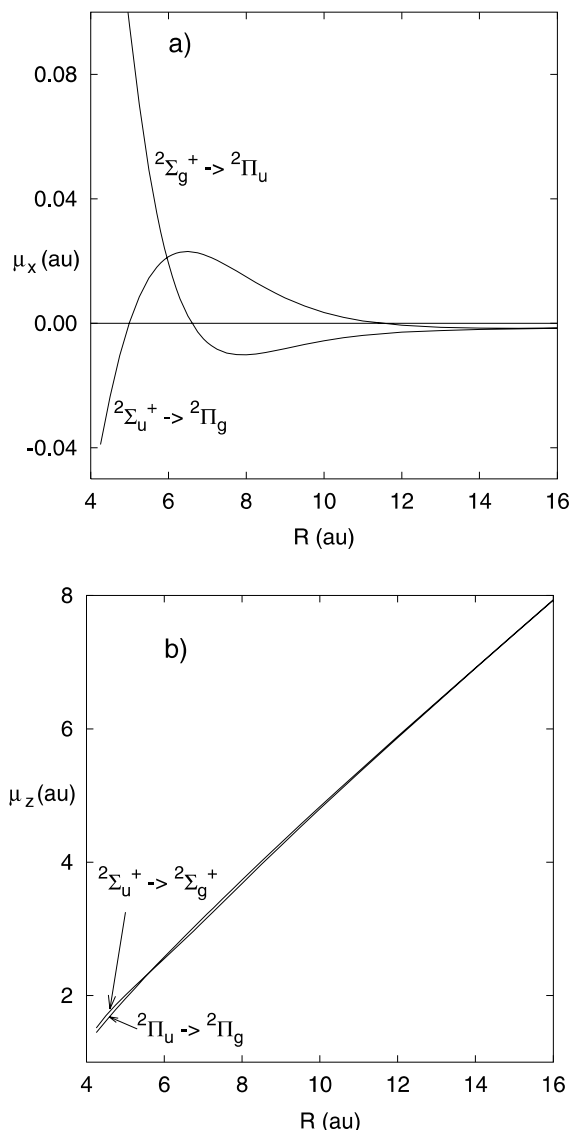


Fig. 3. (a) Perpendicular (μ_x) and (b) parallel (μ_z) transition dipole moments without spin-orbit coupling.

provide the spectroscopic constants which are presented in Table 3 together with the experimental data from Ref. [4] (in parenthesis). The lowest 10–20 vibrational levels for each electronic state were used in fitting. For the three state $A^2\Sigma_{1/2u}^+$ ($I(1/2)_u$), $B^2\Pi_{3/2g}^+$ ($I(3/2)_g$) and $C^2\Pi_{1/2u}^+$ ($II(1/2)_u$), Lu et al. [4] published the positions of vibration peaks for 57, 20 and 27 vibrational

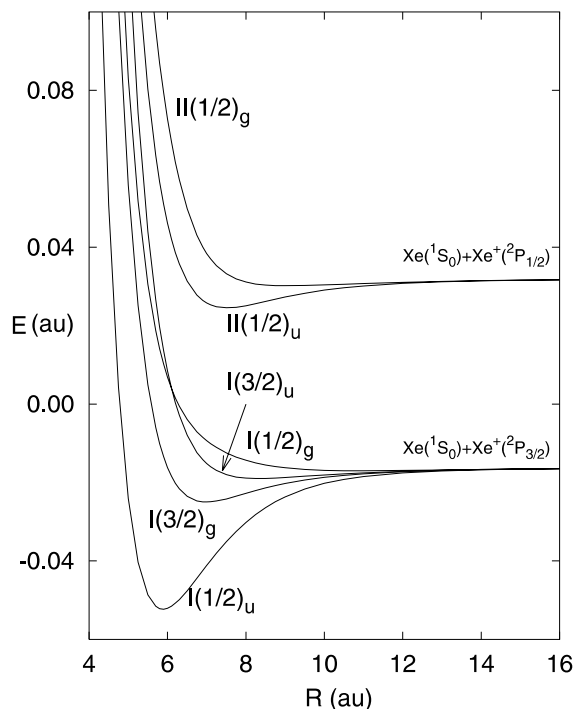


Fig. 4. Potential energy curves for Xe_2^+ with spin-orbit coupling.

states, respectively. In Fig. 6 we compare the experimental values of the vibrational spacings $\Delta G_v = G(v+1) - G(v)$ with the calculated vibrational spacing. As can be seen, our ab initio results look like a least square fitting of the experimental spacing, over the whole range of vibrational levels, and for the three potentials, thus indicating an overall excellent agreement.

We can conclude that the agreement of the calculated data with those derived from experiments is very good and the only significant discrepancy is the value of dissociation energy of the $D^2\Sigma_{1/2g}^+$ ($II(1/2)_g$) state. Our calculated value of 365 cm^{-1} is far from the value 842 cm^{-1} predicted on the basis of the analysis of high resolution photoelectron spectroscopy experiments [4]. However, it is close to the other (older) experimental and theoretical results (see Table VIII in Ref. [4]).

In order to evaluate the mutual relative vertical positions of the energy curves we present as well in Table 3 the T_e values with respect to the ground

Table 2

Potential energy curves of Xe_2^+ assuming an atomic SO coupling in au

R	$I(1/2)_u$	$I(3/2)_g$	$I(3/2)_u$	$I(1/2)_g$	$\Pi(1/2)_u$	$\Pi(1/2)_g$
4.25	0.124476	0.268018	0.387731	0.296455	0.421569	0.440943
4.50	0.051024	0.169569	0.265950	0.197864	0.300129	0.337233
4.75	0.004525	0.101951	0.179144	0.129839	0.213730	0.256495
5.00	−0.023813	0.056070	0.117710	0.083370	0.152771	0.195592
5.25	−0.040058	0.025378	0.074501	0.051919	0.110107	0.150213
5.50	−0.048401	0.005179	0.044271	0.030769	0.080494	0.116450
5.70	−0.051333	−0.005681	0.026859	0.018994	0.063623	0.095834
5.80	−0.051920	−0.009782	0.019900	0.014382	0.056951	0.087258
5.90	−0.052058	−0.013163	0.013910	0.010453	0.051257	0.079679
6.00	−0.051830	−0.015928	0.008764	0.007104	0.046415	0.072994
6.10	−0.051308	−0.018167	0.004351	0.004243	0.042314	0.067109
6.20	−0.050552	−0.019959	0.000575	0.001795	0.038858	0.061942
6.30	−0.049616	−0.021372	−0.002647	−0.000307	0.035961	0.057416
6.50	−0.047370	−0.023290	−0.007723	−0.003691	0.031551	0.050022
6.75	−0.044191	−0.024451	−0.012095	−0.006804	0.028023	0.043291
6.90	−0.042224	−0.024697	−0.013941	−0.008255	0.026683	0.040300
7.00	−0.040922	−0.024727	−0.014922	−0.009092	0.026038	0.038658
7.10	−0.039640	−0.024675	−0.015737	−0.009842	0.025555	0.037256
7.25	−0.037774	−0.024477	−0.016698	−0.010830	0.025082	0.035536
7.50	−0.034864	−0.023937	−0.017768	−0.012181	0.024797	0.033480
7.75	−0.032245	−0.023260	−0.018368	−0.013246	0.024930	0.032159
8.00	−0.029930	−0.022539	−0.018661	−0.014089	0.025310	0.031337
8.25	−0.027912	−0.021830	−0.018758	−0.014756	0.025822	0.030848
8.50	−0.026169	−0.021165	−0.018732	−0.015281	0.026391	0.030579
8.75	−0.024675	−0.020558	−0.018632	−0.015692	0.026966	0.030451
9.00	−0.023402	−0.020016	−0.018492	−0.016009	0.027520	0.030415
9.50	−0.021406	−0.019118	−0.018166	−0.016434	0.028504	0.030488
10.00	−0.019981	−0.018440	−0.017846	−0.016663	0.029295	0.030642
10.50	−0.018966	−0.017931	−0.017561	−0.016766	0.029907	0.030815
11.00	−0.018238	−0.017545	−0.017314	−0.016787	0.030378	0.030985
12.00	−0.017321	−0.017010	−0.016922	−0.016698	0.031023	0.031289
13.00	−0.016817	−0.016679	−0.016645	−0.016554	0.031411	0.031525
14.00	−0.016527	−0.016466	−0.016454	−0.016417	0.031652	0.031700
15.00	−0.016349	−0.016323	−0.016319	−0.016304	0.031808	0.031828

$I(1/2)_u$ state together with the experimental values from Ref. [4]. The last column of Table 3 provides the evaluation of the ab initio potential energy curves by another important criterion, the comparison of the experimental ionization energies (IP) with the values calculated as (see Ref. [4])

$$\text{IP}(\text{Xe}_2) = \text{IP}(\text{Xe}) + D_0(\text{Xe}_2) - D_0(\text{Xe}_2^+).$$

The values of ionization energy of $\text{Xe}(^2P_{3/2})$, $\text{IP}(\text{Xe}) = 97834 \text{ cm}^{-1}$, and dissociation energy of the ground state of Xe_2 , $D_0(\text{Xe}_2) = 185 \text{ cm}^{-1}$ are used. It is seen that the maximum error is around 100 cm^{-1} .

3. Conclusion

The presented ab initio calculations yield reliable data for internuclear separation less than 16 au, however, for larger distances, the RCCSD-T method based on a single configuration overestimates the interaction energies and the analytical extrapolation would be more appropriate for use in the applications. An attempt was done to use the multireference ab initio method AQCC [22], recently successfully applied in study of SO_2 system [23], the results were almost identical to the RCCSD-T ones. The calculation of transition di-

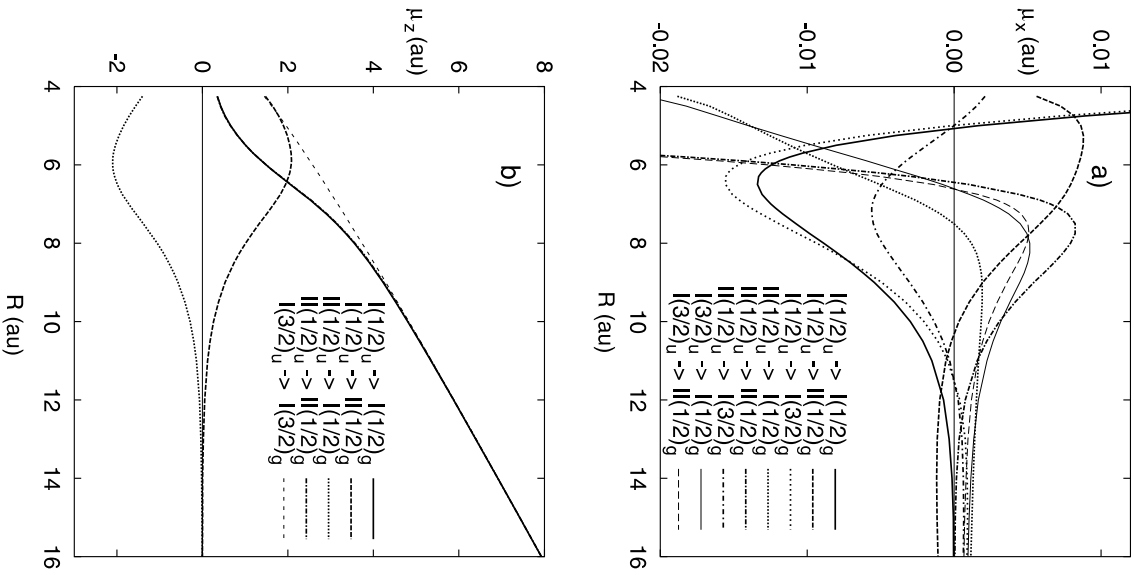


Fig. 5. (a) Perpendicular (μ_x) and (b) parallel (μ_z) transition dipole moments with spin-orbit coupling.

pole moments on the same level of theory insures the homogeneity of the whole set of results.

The present theoretical results are in excellent agreement with available experimental data, particularly in the spectroscopic constants of the ground state, but also in the vibrational spacings in ground and excited states. This encouraging agreement gives confidence in the present data and

Table 3

Spectroscopic constants for Xe_2^+ (experimental data from Refs. [4,5] in parenthesis)

	R_{\min} (au)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e (cm^{-1})	D_0 (cm^{-1})	T_e (cm^{-1})	IP (cm^{-1})
$\text{I}(1/2)_u$	5.885	123.22 (123.41)	0.468 (0.486)	7 904 (7 923)	7 842 (7 861)	0	90 177 (90 158)
$\text{I}(3/2)_g$	6.982	58.74 (58.36)	0.508 (0.484)	1 905 (1 822)	1 876 (1 793)	5 998 (6 101)	96 143 (96 226)
$\text{I}(3/2)_u$	8.306	26.53 (23.1)	0.425 (0.57)	595	582 (437)	7 308	97 437 (97 582)
$\text{I}(1/2)_g$	10.912	9.29	0.102	162	158	7 741	97 861
$\text{II}(1/2)_u$	7.526	50.22 (49.96)	0.421 (0.458)	1 602 (1 472)	1 577 (1 447)	16 867 (16 990)	107 008 (107 109)
$\text{II}(1/2)_g$	9.019	18.18 (<30)	0.310	368	359 (842)	18 100	108 226 (107 714)

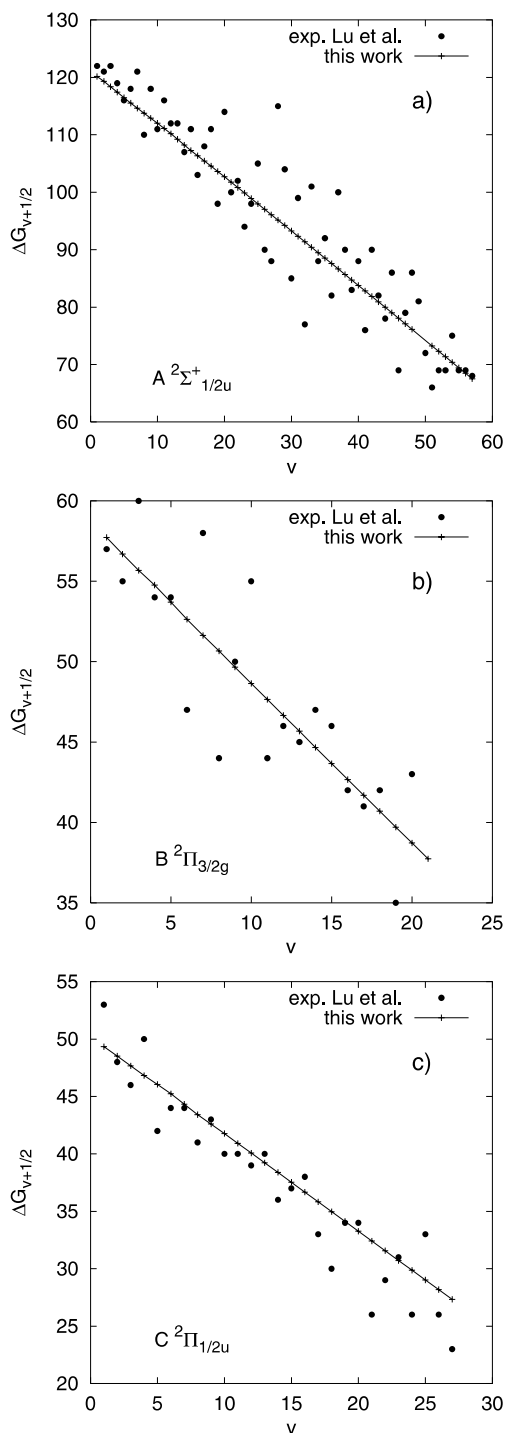


Fig. 6. The spacing of the vibrational levels of the (a) $A^2\Sigma_{1/2u}^+$, (b) $B^2\Pi_{3/2g}$ and (c) $C^2\Pi_{1/2u}$ electronic states of Xe_2^+ . Comparison of the calculation with experiment.

their use in further spectroscopic and dynamical studies of Xe_n^+ clusters using DIM models. Absorption spectra have been measured for various Xe_n^+ clusters while their theoretical simulation [24] relies on potential curves derived from experiments [25]. Improved potentials and transition dipole moments, as produced here, can be useful in that context, in particular beyond the application of the recently proposed point charge model [8,10,19].

Acknowledgements

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