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All-electron ab initio investigations of the three lowest-lying electronic states of the RuC molecule

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Abstract

The three lowest-lying electronic states of RuC, $^1\Sigma^+$, $^3\Delta$, and $^1\Delta$, have been investigated by performing all-electron ab initio multi-configuration self-consistent-field (CASSCF) and multi-reference configuration interaction (MRCI) calculations including relativistic corrections. The electronic ground state is derived as $^1\Sigma^+$ with the spectroscopic constants $r_e = 1.616$ Å and $\omega_e = 1085$ cm^{-1}. The lowest-lying excited state, $^3\Delta$, has $r_e = 1.632$ Å, $\omega_e = 1064$ cm^{-1}, and $T_e = 912$ cm^{-1}. These results are consistent with recent spectroscopic values. The chemical bonds in all three lowest-lying states are triple bonds composed of one σ and two π bonds. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In previous work on RuC [1] we have investigated 28 electronic states by carrying out Hartree–Fock and valence configuration interaction (HF valence CI) calculations. The ground state was determined as $^3\Delta$, and two low-lying excited states, $^1\Sigma^+$ and $^1\Delta$, were identified. On basis of the results obtained, the electronic spectra observed by Scullman and Thelin [2,3] were assigned as transitions between the $^3\Delta$ ground state and two close-lying excited states, $^3\Pi$ and $^3\Phi$. The chemical bonds in the three lowest-lying states, $^1\Sigma^+$, $^3\Delta$, and $^1\Delta$, were determined to be triple bonds, each composed of one σ bond and two π bonds. The 5s electron of Ru was found to be essentially non bonding, located in a singly occupied non-bonding orbital. The molecule was found to be polar with charge transfer from Ru to C. The dissociation energy of the molecule, D_0^0, was determined using high-temperature mass spectrometric measurements as 612.4 ± 10.5 kJ mol$^{-1} = 6.35 \pm 0.11$ eV.

Recently Langenberg et al. [4] have presented their resonant two-photon ionization spectroscopic investigation of jet-cooled RuC molecules. In comparing their results with those obtained in our earlier HF valence CI calculations [1,5–7] it is noted that their now established $^1\Sigma^+$ ground state was calculated to lie 4275 cm^{-1} above the $^3\Delta$ state that was predicted as the ground state. Langenberg et al. also assign the bands observed by Scullman and Thelin [2,3]. Five of the six bands previously assigned by us [1] coincide with the assignment proposed in [4]. One band, the 7909 Å band, we assigned as a $^3\Pi_0$–$^3\Delta_1$ transition while Langenberg et al. propose it to be a $^3\Phi_3$–$^3\Delta_2$ transition.

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The new spectroscopic data have induced us to carry out the present investigation, where we have performed all-electron ab initio multi-configuration self-consistent-field (MCSCF) calculations within the complete active space self-consistent-field approach (CASSCF). The three lowest-lying states have been further investigated by performing multi-reference configuration interaction (MRCI) calculations. The relativistic effects have been considered by performing perturbation calculations of the one-electron Darwin contact term and of the relativistic mass-velocity term. The calculations have been carried out using the program system MOLCAS, version 4 [8]. Furthermore, the effect of spin–orbit coupling on the low-lying states has been considered by performing approximate perturbation treatments.

The level of the computational work used in the present investigation is analogue to that in our investigations of the carbide molecules, MoC [9] and PdC [10]. For these molecules good agreement has been achieved with the spectroscopic data that have appeared later for MoC [11] and simultaneously for PdC [12].

2. Basis sets and atomic calculations

The basis sets consisted of contracted Gaussian type functions. For the Ru atom we have used Huzinaga's $(17s, 11p, 8d)$ basis set [13], but extended by one s function with exponent 0.015, by three p functions with exponents 0.1827, 0.08209, and
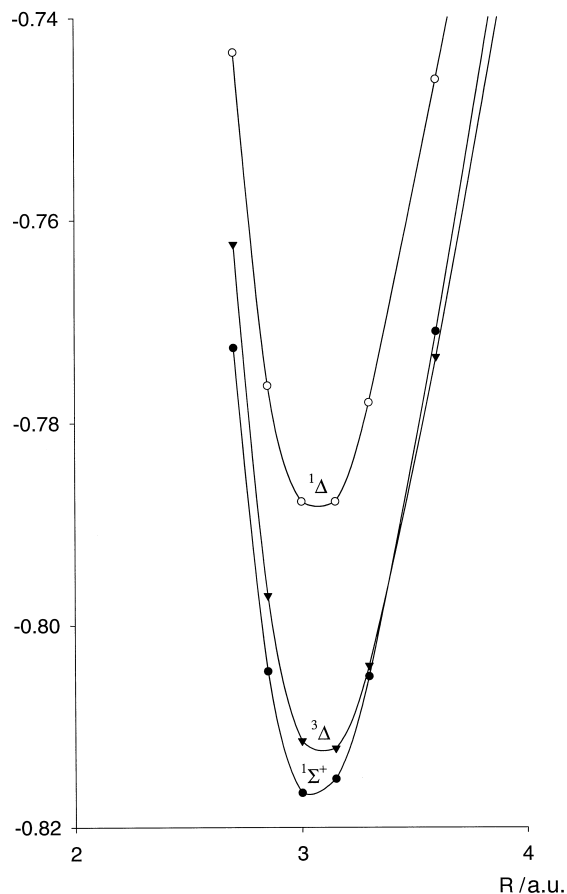

Fig. 1. Potential energy curves of the three lowest-lying states of the RuC molecule as derived from MRCI calculations including relativistic corrections, i.e. the one-electron Darwin contact term and the mass–velocity term.

0.03337, and by one d function with exponent 0.09072. Finally, two f polarization functions with exponents 0.965 and 0.3679 were added. The primitive basis set $(18s, 14p, 9d, 2f)$ was contracted to $(11s, 9p, 5d, 2f)$ using a segmented contraction scheme. In the contracted basis the valence orbitals, 5s, 5p, and 4d are all represented by triple-zeta functions while all core orbitals are represented by double-zeta functions. For the C atom we have used Huzinaga's $(10s, 6p)$ basis [14], but augmented with a d polarization function with exponent 0.75. The basis set for the C atom was contracted to $(4s, 3p, 1d)$, resulting in double-zeta representation of the s func-

Table 1
Relative energies for the $^5F(4d)^7(5s)^1$ ground term and of the excited terms, $^3F(4d)^7(5s)^1$ and $^3F(4d)^8$, of the Ru atom

Method	Relative energy (eV)		
	$^5F(4d)^7(5s)^1$	$^3F(4d)^7(5s)^1$	$^3F(4d)^8$
Experimental[a]	0.00	0.78	1.09
CASSCF without relativistic corrections	0.00	0.83	1.71
CASSCF with relativistic corrections	0.00	0.98	2.32
MRCI without relativistic corrections	0.00	0.64	0.85
MRCI with relativistic corrections	0.00	0.78	1.49

[a]Ref. [15].

Table 2
Spectroscopic constants of the lowest-lying electronic states of the RuC molecule as derived from the results of MRCI calculations. Also included are the spectroscopic constants derived for the relativistic corrected states including the spin–orbit coupling

State	Excluding relativistic corrections				Including relativistic corrections					
	equilibrium distance, r_e (Å)	vibrational frequency, ω_e (cm^{-1})	transition energy, T_e (cm^{-1})	dissociation energy[a], D_e (eV)	equilibrium distance, r_e (Å)	vibrational frequency, ω_e (cm^{-1})	transition energy, T_e (cm^{-1})	dissociation energy[a], D_e (eV)	gross atomic charge on Ru	dipole moment, μ (D)
$^1\Sigma^+$	1.614	1070	0	5.84	1.616	1085	0	5.60	−0.01	4.018
$^3\Delta$	1.632	1041	5797	5.13	1.632	1064	912	5.49	−0.04	0.897
$^1\Delta$	1.619	1061	10129	4.59	1.618	1086	6062	4.85	−0.06	0.069
$^3\Delta_3$					1.632	1064	45			
$^3\Delta_2$					1.632	1064	771			
$^3\Delta_1$					1.632	1064	1779			
$^1\Delta_2$					1.618	1086	6204			

[a] Derived as the difference between the total molecular energy at the equilibrium distance and the sum of the energies of the atoms.

tions, triple-zeta representation of the 2p function, and a d polarization function.

Table 1 shows the energies of the excited terms of Ru, $^3F(4d)^7(5s)^1$ and $^3F(4d)^8$, relative to that of the $^5F(4d)^7(5s)^1$ ground term based on CASSCF and MRCI calculations. The calculated splitting between the $^5F(4d)^7(5s)^1$ ground term and the $^3F(4d)^7(5s)^1$ excited term derived in the MRCI calculations including the relativistic corrections is identical to the experimental value derived from Moore's Tables [15] by averaging over the spin–orbit components. As expected the splitting between the ground term and the $^3F(4d)^8$ term is not reproduced to the same accuracy, but the right ordering is obtained.

The basis set used for the Ru atom in the present investigation is analogues to those used for Mo and Pd in our recent work on MoN [16] and PdC [10].

3. Results of CASSCF calculations on the RuC molecule

In the CASSCF calculations the core orbitals, i.e. the 1s, 2s, 3s, 4s, 2p, 3p, and 3d of Ru and the 1s orbital of C, were kept fully occupied, while the valence orbitals 5s and 4d of Ru and 2s and 2p of C, have been included in the active space. The calculations have been performed in the subgroup C_{2v} of the full symmetry group $C_{\infty v}$ of the RuC molecule. The number of configurations included in the CASSCF calculations for the $^3\Delta$ state amounts to 5196, 3588 for the $^1\Sigma^+$ state, and to 3392 for the $^1\Delta$ state.

The influence of the relativistic effects have been included by carrying out perturbation calculations to derive values for the one-electron Darwin contact term and for the mass–velocity term.

The CASSCF calculations have been performed as functions of the internuclear distance, i.e. for the distances 2.70, 2.85, 3.00, 3.15, 3.30, 3.60, 3.90, 4.20, 4.50, 5.00, 7.00, and 12.00 a.u. The spectroscopic constants were obtained from the results of the calculations by solving the Schrödinger equation for the nuclear motion numerically.

Without relativistic corrections the ground state determined in the CASSCF calculations is determined to be $^1\Sigma^+$, and this state is separated from the states $^3\Delta$ and $^1\Delta$ by 2818 and 7008 cm^{-1}, respectively. When the relativistic corrections are included, the $^3\Delta$ is the ground state, and this state is separated by 1822 cm^{-1} from the $^1\Sigma^+$ state and by 5059 cm^{-1} from the $^1\Delta$ state. The dissociation energy, D_e, of the $^1\Sigma^+$ state of the RuC molecule is derived by subtracting the molecular energy at the equilibrium distance from that at 12 a.u. The value for D_e is obtained as 5.97 eV without relativistic corrections, and as 5.90 eV including the relativistic corrections. However, this is the adiabatic dissociation energy. The corresponding diabatic dissociation energy is 5.14 eV without relativistic corrections and 4.91 eV including the relativistic corrections.

4. Results of MRCI calculations

The molecular orbitals optimized in the CASSCF calculations have been used as basis in the MRCI calculations for the three lowest-lying states, $^1\Sigma^+$, $^3\Delta$, and $^1\Delta$, of RuC. The reference configurations used in the MRCI calculations were chosen as those with the largest coefficients in the CASSCF calculations. For the $^1\Sigma^+$ state 41 reference configurations

Table 3

The contributions of the major configurations to the MRCI wavefunctions describing the $^1\Sigma^+$ ground state and the lowest-lying excited states of the RuC molecule as functions of the internuclear distance

State	Valence shell configuration							Contribution of valence shell configuration (%)								
	10σ	11σ	12σ	13σ	5π	6π	2δ	internuclear distance (a.u.)								
	(C s)	(σ)	(Ruσ)	(σ^*)	(π)	(π^*)		2.70	2.85	3.00	3.15	3.30	3.60	3.90	4.20	4.50
$^1\Sigma^+$	2	2	0	0	4	0	4	86	84	82	80	78	73	66	56	43
$^3\Delta$	2	2	1	0	4	0	3	86	85	83	81	79	74	67		
$^1\Delta$	2	2	1	0	4	0	3	86	85	83	81	78	72	61	50	40

Table 4

Occupations in the natural orbitals for the lowest-lying electronic states of RuC as derived in MRCI calculations. Also shown are the dipole moments at the internuclear distance 3.15 a.u.

State	Internuclear distance (a.u.)	Dipole moment (D)	Population in						
			10σ (C s)	11σ σ	12σ (Ru σ)	13σ (σ^*)	5π (π)	6π (π^*)	2δ
$^1\Sigma^+$	3.15	4.075	1.96	1.92	0.09	0.01	3.77	0.22	3.94
$^3\Delta$	3.15	1.050	1.97	1.93	0.99	0.05	3.76	0.22	2.98
$^1\Delta$	3.15	0.242	1.97	1.93	0.99	0.06	3.76	0.22	2.97

were included, 40 for $^3\Delta$ state, and 21 for $^1\Delta$ state. In the MRCI calculations all single and double excitations were allowed from the reference configurations. This produced a total of 1 570 500, 2 879 882, and 1 306 699 configurations for the states $^1\Sigma^+$, $^3\Delta$, and $^1\Delta$, respectively. For all three states the calculations have been performed at the internuclear distances 2.70, 2.85, 3.00, 3.15, 3.30, 3.60, 3.90, 4.20, and 4.50 a.u. The potential energy curves obtained in the MRCI calculations including the relativistic corrections are shown in Fig. 1.

The spectroscopic constants were obtained by solving the Schrödinger equation for the nuclear motion numerically, and the results, both excluding and including the relativistic effects are displayed in Table 2. It is noted that the ground state is identified as $^1\Sigma^+$, and the separation between this state and the $^3\Delta$ state is reduced from 5797 to 912 cm^{-1} when the relativistic effects are taken into account.

The dissociation energy has been derived by subtracting the energy of the molecule at the equilibrium distance from the sum of the energies of the atoms in their ground states determined in MRCI calculations. Without the relativistic corrections the value of D_e is

5.84 eV and of D_0 5.77 eV. When the relativistic corrections are included D_e is derived as 5.60 eV and D_0 as 5.53 eV.

The dipole moment and the gross atomic charge on Ru have been derived at the relativistic equilibrium distance by interpolation. For the $^1\Sigma^+$ ground state the gross atomic charge on Ru amounts to -0.01 e, and the dipole moment to 4.018 D. For the excited states, $^3\Delta$ and $^1\Delta$, the gross atomic charges are -0.04 and -0.06 e, and the dipole moments 0.897 and 0.069 D, respectively.

Table 3 shows the contributions of the major configurations in the MRCI wavefunctions for the three lowest-lying states, $^1\Sigma^+$, $^3\Delta$, and $^1\Delta$. The major configuration for the $^1\Sigma^+$ state is $(10\sigma)^2(11\sigma)^2(5\pi)^4(2\delta)^4$, and for both states, $^3\Delta$ and $^1\Delta$, it is $(10\sigma)^2(11\sigma)^2(12\sigma)^1(5\pi)^4(2\delta)^3$. Thus, the states, $^3\Delta$ and $^1\Delta$, are due to triplet and singlet couplings of the orbitals 12σ and 2δ, respectively. It is noted that the weights of the major configurations for all three states amount to slightly more than 80% near the equilibrium distances.

Tables 4 and 5 show selected results of population analyses for the lowest-lying states. Table 4 reports

Table 5

Results of population analysis for the lowest-lying electronic states of RuC based on the results of the MRCI calculations. Also included are the gross atomic charges and the total number of d electrons on Ru at the internuclear distance 3.15 a.u.

State	Internuclear distance (a.u.)	Gross atomic charge on Ru	Number of d electrons on Ru	Population								
				Ru						C		
				$4d\sigma$	$4d\pi$	$4d\delta$	$5s$	$5p\sigma$	$5p\pi$	$2s$	$2p\sigma$	$2p\pi$
$^1\Sigma^+$	3.15	0.01	7.65	1.28	2.42	3.95	0.14	0.10	0.04	1.73	0.71	1.51
$^3\Delta$	3.15	-0.03	6.91	1.37	2.57	2.98	0.82	0.18	0.05	1.78	0.79	1.35
$^1\Delta$	3.15	-0.05	6.89	1.38	2.54	2.98	0.85	0.19	0.05	1.79	0.74	1.38

the approximate occupations of the natural valence orbitals and the dipole moments at the internuclear distance 3.15 a.u. From Table 5 it is especially noted that the states $^3\Delta$ and $^1\Delta$ both originate from the $(4d)^7(5s)^1$ configuration of Ru, whereas the $^1\Sigma^+$ ground state has substantial admixture of the $(4d)^8$ configuration of the Ru atom. The larger populations of the 5s orbital of Ru in the states $^3\Delta$ and $^1\Delta$ as compared to that of the $^1\Sigma^+$ ground state is consistent with the much larger relativistic corrections for these states.

5. Spin–orbit coupling

The spin–orbit coupling has been considered by carrying out an approximate perturbation treatment
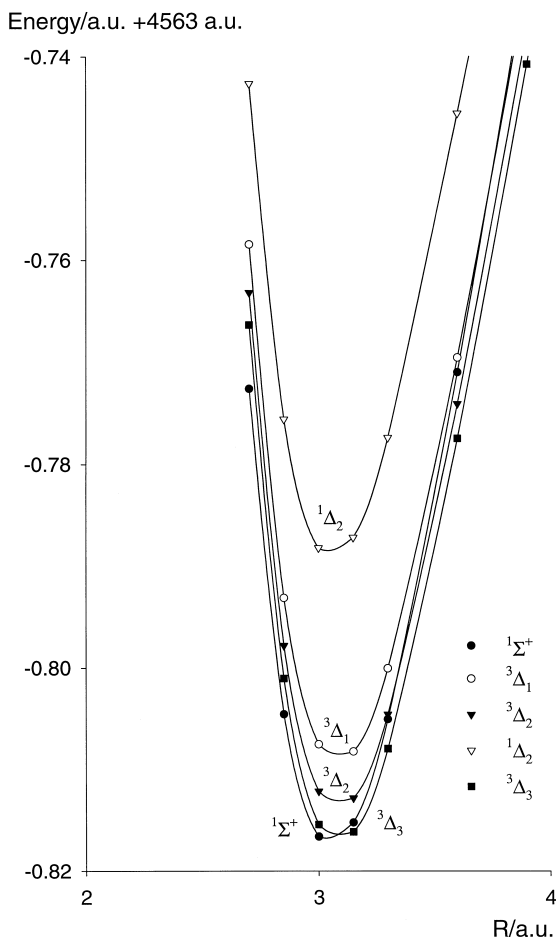
Energy/a.u. +4563 a.u.

Fig. 2. Potential energy curves of the lowest-lying spin–orbit coupled electronic states of the RuC molecule.

using the operator $H' = \sum \xi(r_i) \bar{l}_i \cdot \bar{r}_i$. It is assumed that the radial integrals ξ are all equal, and the value of the spin–orbit coupling constant has been derived as 867 cm^{-1} from Moore's Tables [15] based on the splittings of the $^5F(4d)^7(5s)^1$ ground term. The results of the spin–orbit coupling treatment is shown in Table 2 and Fig. 2. When the spin–orbit coupling is included, the $^1\Sigma^+$ ground state is separated from the $^3\Delta_3$ state by only 45 cm^{-1}. This splitting is completely dependent on the value for the spin–orbit coupling constant.

6. Discussion

Based on the MRCI calculations including relativistic corrections the transition energy between the states $^1\Sigma^+$ and $^3\Delta$ is derived as 912 cm^{-1}. This value agrees well with the transition energy 850 cm^{-1} between the states $^1\Sigma^+$ and $^3\Delta_2$ determined by Langenberg et al. [4]. When the spin–orbit coupling is taken into account the splitting between the $^1\Sigma^+$ and $^3\Delta_3$ states is reduced to 45 cm^{-1}. Although this value is close to the value of 76 cm^{-1} determined experimentally by Langenberg et al. [4], it would not be safe to predict the electronic ground state of RuC with certainty on basis of the present theoretical results. The equilibrium distances derived for the states $^1\Sigma^+$ and $^3\Delta$, 1.616 and 1.632 Å, respectively, also agree well with the r_0 values, 1.608 and 1.635 Å, measured by Langenberg et al. The vibrational frequency, $\Delta G_{1/2}$, they determined as 1 029.587(20) for $^1\Sigma^+$ for the ^{102}Ru^{12}C isotomer. This value is lower than our calculated ω_e value by 55 cm^{-1}.

The dissociation energy derived in the present investigation is lower than our previously measured value by ~ 0.82 eV [1]. This indicates the difficulties involved in theoretical determination of this property.

The ionization potential of RuC has been determined in our previous mass spectrometric investigation by the linear extrapolation method as 8.4 ± 0.7 eV, using the ionization energies of atomic silver (7.57 eV) and rhodium (7.46 eV) [15] to calibrate the electron energy scale. This experimental value places the ionization energy of RuC close to the upper limit

of the 6.42–8.01 eV range established by Langenberg et al. [4].

The valence orbitals of RuC can be characterized as follows: the 10σ orbital is basically the C $2s$ orbital. The 11σ orbital is mainly the bonding combination of the C $2p\sigma$ and the Ru $4d\sigma$ orbital. The 13σ orbital is the corresponding anti-bonding orbital. The orbital 12σ is primarily a non-bonding orbital located on Ru, mostly the Ru $5s$ but with some admixture of Ru $5p$ that causes the orbital to be polarized away from the internuclear region. The 5π orbital is the bonding combination of the Ru $5d\pi$ and the C $2p\pi$, polarized towards Ru. The 6π orbital is the corresponding anti-bonding orbital, polarized towards C. Finally, the 2δ orbitals are the Ru $4d\delta$.

The results presented in Tables 3–5 are consistent with a molecular orbital diagram where the lowest-lying valence orbital is essentially the C $2s$ orbital, i.e. 10σ. The next higher-lying orbitals are the bonding orbitals 5π and 11σ. Thereafter follow the non-bonding orbitals, 2δ and 12σ, at higher energy are the anti-bonding orbitals, 6π and 13σ. Since the states $^1\Sigma^+$ and $^3\Delta$ are almost degenerate, the orbitals 2δ and 12σ must be almost degenerate. This orbital diagram is in agreement with that proposed in our earlier work [1,6,7]. The chemical bonds in all three lowest-lying states are approximately triple bonds composed of two π bonds and one σ bond as was also suggested in our earlier work [1,5–7].

With respect to orbital occupations the results of the population analyses presented in Tables 4 and 5 are basically in agreement with the results obtained in our earlier work on RuC [1]. However, in one respect the results differ. In our earlier work the RuC molecule was found to be polar with charge transfer from Ru to C, but in the present work the gross atomic charge derived in the Mulliken population analyses indicates that the molecule is practically non polar. This, however, is inconsistent with the dipole moment that has been derived as 4.018 D for the ground state. The value of the dipole moment indicates that the molecule is polar with substantial charge transfer from Ru to C. Therefore, our results indicate that the gross atomic charge derived in the Mulliken population analyses in the present work is not adequate. The excited states, $^3\Delta$ and $^1\Delta$, both have much smaller dipole moments than the ground state. This is consistent with their much larger population of the $5s$, $5p$ hybrid orbital of Ru that cause charge to be removed from the internuclear region in the excited states.

7. Conclusions

In the present work we have investigated the three lowest-lying electronic states, $^1\Sigma^+$, $^3\Delta$, and $^1\Delta$, of RuC by performing all-electron ab initio MCSCF (CASSCF) and MRCI calculations. The electronic ground state of the RuC molecule has been derived as $^1\Sigma^+$ in agreement with the recent experimental work by Langenberg et al. [4].

The spectroscopic constants of the RuC molecule in the $^1\Sigma^+$ ground state have been derived as $r_e = 1.616$ Å and $\omega_e = 1085$ cm^{-1}. These values compare favorably with the experimental values of 1.608 Å for r_0 and of 1030 cm^{-1} for ω_e [4]. The dissociation energy, D_e is derived as 5.60 eV, and D_0 as 5.53 eV. The value for D_0 is less than our previously determined experimental value by 0.82 eV.

The leading configuration of the $^1\Sigma^+$ ground state is $(10\sigma)^2(11\sigma)^2(5\pi)^4(2\delta)^4$. The chemical bonds in all three lowest-lying states are triple bonds consisting of two π bonds and one σ bond. This description of the chemical bond in RuC is consistent with that of our earlier work [1,5–7].

Acknowledgements

References

[1] I. Shim, H.C. Finkbeiner, K.A. Gingerich, J. Phys. Chem. 91 (1987) 3171.

[2] R. Scullman, B. Thelin, Phys. Scr. 3 (1971) 19.

[3] R. Scullman, B. Thelin, Phys. Scr. 5 (1972) 201.

[4] J.D. Langenberg, R.S. DaBell, L. Shao, D. Dreessen, M.D. Morse, J. Chem. Phys. 109 (1998) 7863.

[5] I. Shim, K.A. Gingerich, Surf. Sci. 156 (1985) 623.

[6] I. Shim, in: J. Avery, J.P. Dahl, A.E. Hansen (Eds.), Understanding Molecular Properties, Reidel, Amsterdam, 1987, p. 555.

[7] K.A. Gingerich, I. Shim, in: J.F.J. Todd (Ed.), Advances in Mass Spectrometry, Wiley, New York, 1986, p. 1051.

[8] K. Andersson, M.R.A. Blomberg, M.P. Fülscher, G. Karlström, R. Lindh, P.-Å. Malmquist, P. Neogrády, J. Olsen, B.O. Roos, A.J. Sadley, M. Schütz, L. Seijo, L. Serrano-Andrés, P.E.M. Siegbahn, P.O. Widmark, MOLCAS version 4, Lund University, Lund, 1997.

[9] I. Shim, K.A. Gingerich, J. Chem. Phys. 106 (1997) 8093.

[10] I. Shim, K.A. Gingerich (submitted).

[11] D.J. Brugh, T.J. Ronningen, M.D. Morse, J. Chem. Phys. 109 (1998) 7851.

[12] J.D. Langenberg, L. Shao, M.D. Morse, J. Chem. Phys. (in press).

[13] S. Huzinaga, J. Chem. Phys. 66 (1977) 4245.

[14] S. Huzinaga, J. Chem. Phys. 42 (1965) 1293.

[15] C.E. Moore, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., Washington, DC, 35/V.III, 1971.

[16] I. Shim, K.A. Gingerich, J. Mol. Spectrosc. (Theochem) 460 (1999) 123.