Vibrational Constants and Binding Energies for the Low-Lying Electronic States of Sr^+CO_2 from Photodissociation Spectroscopy

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By use of photodissociation spectroscopy of mass-selected ions, vibrationally resolved electronic spectra of the Sr^+CO_2 complex are recorded in two energy regions, 20 780−22 990 and 16 210−17 550 cm^{-1}, correlating to the Sr^+ $5^2P \leftarrow 5^2S$ and $4^2D \leftarrow 5^2S$ transitions, respectively. The spectra are analyzed to obtain the vibrational constants and dissociation energies of the molecular states. The observed spin−orbit splitting indicates a linear complex in agreement with theoretical calculations. The results are compared with similar systems and explained in the framework of electrostatic interactions.

Introduction

A metal ion interacting with an atom or a molecule in the gas phase constitutes the most elementary system for understanding the structure and bonding of larger molecules. Many features in clusters, biomolecules, and the condensed phase evolve from the properties of these small systems. Therefore, they serve as prototypes for studying a variety of physical and chemical processes such as optical absorption, electronic energy transfer, reactivity, catalysis, etc.

Over the last years the photodissociation spectroscopy of mass-selected metal ion−atom/molecule complexes has been proved to be a powerful tool in obtaining information about the potential energy surfaces and the spectroscopic constants of electronic excited states. This technique has been applied by several groups[1−7] and has given a large amount of data concerning the binding and interaction within such molecules.

Complexes between alkaline earth metal ions and atoms or molecules are of particular interest because of their simple electronic configuration, which allows us to perform ab initio calculations and comparisons with experimental work. Additionally, these systems exhibit an atomiclike strong s−p dipole transition, which is energetically accessible by the existing laser systems, and therefore they are ideal for experimental investigations.

Using photodissociation spectroscopy of mass-selected ions, our group has systematically investigated in the last years the binding of Sr^+ with noble gases Ne, Ar, Kr, and Xe.[9−12] We have obtained spectra that correspond to transitions from the electronic ground state $X^2\Sigma^+$ to the excited $^2\Pi$ states associated with the Sr^+ 5p orbital. Recently, we have studied the excited states of the Sr^+CO complex,[13,14] and we have recorded spectra of states correlating to the Sr^+ 5^2P and 4^2D spectroscopic terms. Furthermore, we investigated theoretically (electronic configuration interaction calculations) these spectra, obtaining information about the corresponding excited states.

In this paper we present the photodissociation spectra of Sr^+CO_2 in the laser energy regions 20 780−22 990 and 16 210−17 550 cm^{-1}. For this system there exist ab initio calculations from Sodupe et al.[15] concerning the low-lying electronic states. This allows a comparison between our experimental results and theoretical ones. We discuss the results in the framework of electrostatic interactions and also compare the binding between Sr^+ and several noble gas atoms or molecules.

Experimental Section

The molecular beam apparatus used in these experiments has been described in detail previously.[10,11] In short, $Sr^+(CO_2)_n$ clusters are formed by mixing the plasma plume, produced by laser ablation of a strontium metal rod, with the expansion of CO_2 from a pulsed nozzle. The cationic complexes produced are accelerated by a pulsed double field time-of-flight (TOF) device toward a reflectron assembly. The backward-reflected ions are spatially focused to a microchannel plate detector, where TOF mass spectra are recorded with a computer-controlled digital storage oscilloscope. During their flight from the acceleration region to the reflectron assembly, the Sr^+CO_2 ions are selected through a mass gate from the whole cluster size distribution. Closely behind the mass gate a laser beam from a tunable OPO laser system (Spectra Physics MOPO SL 730-10, 10 Hz pulse rate, 0.2 cm^{-1} bandwidth) intersects the ion beam perpendicularly. In the case of photodissociation, the parent and the fragments are separated in the TOF spectrum by the aid of the reflectron. The photodissociation spectrum is obtained by measuring the intensity ratio of the ionic fragments to the total signal and normalized by the laser intensity for each laser wavelength.

Results

A. Electronic States. Sodupe et al.[15] have calculated the electronic structure of Sr^+CO_2 complex by ab initio methods. They found a linear structure for the complex in electronic ground state. Furthermore, they have considered the low-lying electronic states of this molecule and have computed the vertical excitation energies. The expected electronic states for such a linear molecule are shown in Figure 1. The ground state of the complex is $X^2\Sigma^+$ and results from the interaction of the Sr^+ 5s orbital with the $^1\Sigma_g{}^+$ ground state of the CO_2 molecule. The first excited electronic states $(1)^2\Delta$, $(1)^2\Pi$, and $(2)^2\Sigma^+$ derive from the interaction of Sr^+ 4d orbitals. The spin−orbit splitting $A_D = 280.3$ cm^{-1} of the atomic 4d orbital results in the atomic

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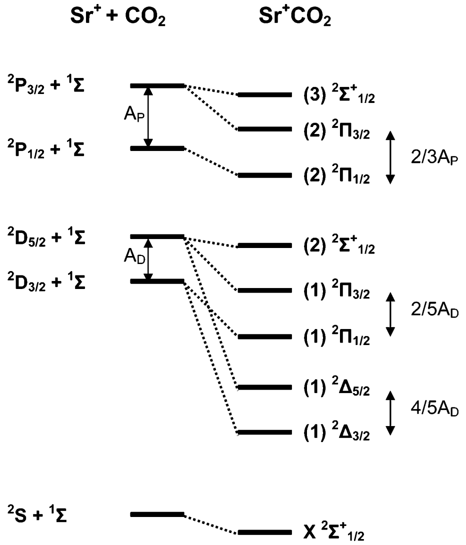

Figure 1. Low-lying electronic states of the linear $Sr^+{-}CO_2$ complex arising from the Sr^+ terms and the $^1\Sigma_g{}^+$ ground state of CO_2. A_D and A_P are the atomic spin−orbit splitting for the Sr^+ 4^2D and 5^2P states, respectively.

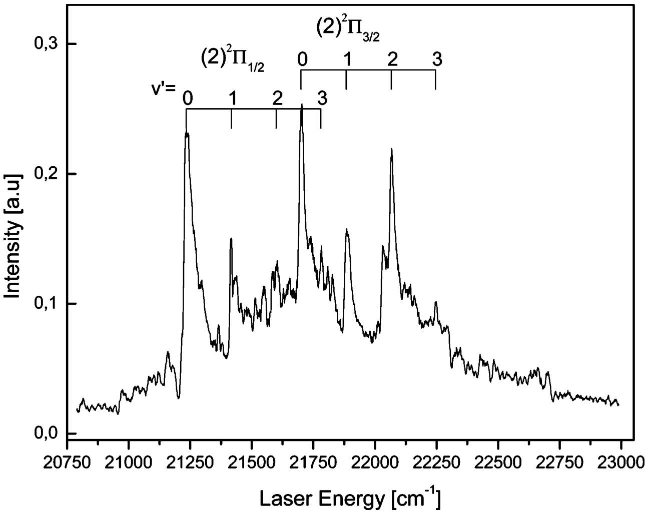

Figure 2. Photodissociation spectrum of Sr^+CO_2 corresponding to $(2)^2\Pi \leftarrow X^2\Sigma^+$ transitions.

$4^2D_{3/2}$ and $4^2D_{5/2}$ states with transition energies 14 555.9 and 14 836.2 cm^{-1}, respectively.[16] The corresponding molecular states are $(1)^2\Delta_{3/2,5/2}$, $(1)^2\Pi_{1/2,3/2}$, and $(2)^2\Sigma^+{}_{1/2}$. In a similar manner, the Sr^+ 5p orbital splits into $5^2P_{1/2}$ and $5^2P_{3/2}$ atomic states separated by $A_P = 801.4$ cm^{-1}. The transition energies of these two states are 23 715.2 cm^{-1} and 24 516.6 cm^{-1}, respectively,[16] and the resulting molecular states are $(2)^2\Pi_{1/2,3/2}$ and $(3)^2\Sigma^+{}_{1/2}$.

B. $(2)^2\Pi \leftarrow X^2\Sigma^+$ Band. Figure 2 shows the experimental photodissociation spectrum of the mass-selected $^{88}Sr^+CO_2$ in the laser energy region 20 780−22 990 cm^{-1}. The spectrum in Figure 2 is measured near the atomic $5^2P \leftarrow 5^2S$ transition and shows two vibrational progressions with four lines each. According to the theoretical results of Sodupe et al.[15] and also the results of similar $Sr^+{-}X$ systems, measured in our laboratory,[9−14] we attributed these progressions to dipole transitions from the $X^2\Sigma^+{}_{1/2}$ ground state to the excited $(2)^2\Pi_{1/2}$ and $(2)^2\Pi_{3/2}$ states.

Both progressions are red-shifted with respect to the Sr^+ transition frequencies (≈24 250 cm^{-1}), indicating that the binding energy for the excited $(2)^2\Pi$ states is greater than that of the ground state. Furthermore, the line shapes exhibit a sharp rising edge at the lower energy side and a shaded "blue" side, characteristic for a shorter equilibrium internuclear distance of the excited state than the one of the ground state.

TABLE 1: Positions and Assignments of the $(2)^2\Pi \leftarrow X^2\Sigma^+$ Transitions

	$^2\Pi_{1/2}$			$^2\Pi_{3/2}$		
v'	$v'' = 0$	$v' = 1$	$\Delta E''_{1/2}$	$v'' = 0$	$v' = 1$	$\Delta E''_{1/2}$
0	21 233.5	21 174.1	59.4	21 699.4	21 649.0	50.4
1	21 416.2	21 365.2	51.0	21 883.7	21 827.4	56.3
2	21 600.1	21 547.5	52.6	22 066.5	22 010.6	55.9
3	21 779.6			22 245.6	22 200.1	45.5
4				22 425.5		

[a] Positions are given in reciprocal centimeters.

Between the main lines of the vibrational progressions there is a background with small peaks, most of which can be attributed to hot bands, that is, transitions originating from the first vibrationally excited level of the ground state.

For absolute line numbering, isotope resolved measurements are necessary. In this case, however, since the first line observed in each progression has the highest intensity we assign it $v' = 0$, as expected from the Franck−Condon principle for a diatomic molecule. If the $Sr^+{-}CO_2$ complex is considered as a pseudodiatomic molecule, which vibrates as an anharmonic oscillator, the spectroscopic constants of the involved states can be determined. The band origin ν_{00}, the vibrational frequency ω_e', and the anharmonicity $\omega_e\chi_e'$ for each excited state are obtained by least-squares fitting of the vibronic positions (Table 1) to the anharmonic oscillator formula:

$$E(v') = \nu_{00} + \omega_e'(v' + {}^1\!/_2) - \omega_e\chi_e'(v' + {}^1\!/_2)^2 - (\omega_e'/2 - \omega_e\chi_e'/4) \quad (1)$$

The values obtained are listed in Table 2.

Provided that the Sr^+CO_2 complex is linear in its ground state, the observed frequency of 185 cm^{-1} can be attributed to $Sr^+{-}CO_2$ stretching vibration. A linear configuration is supported from the observed molecular spin−orbit splitting $\Delta_{so} = 467$ cm^{-1}, which is comparable to 534 cm^{-1} = $2A_P/3$, as expected for a linear Hund's case (a) complex. The ab initio results of Sodupe et al.[15] also show a linear configuration. For a linear complex, the only allowed vibrations are the metal−CO_2 stretching mode and the normal CO_2 vibrational modes: symmetric stretch (1388 cm^{-1}), asymmetric stretch (2349 cm^{-1}), and bending (667 cm^{-1}). No bending motion is deduced from our spectra.

The observed differences between the $v' \leftarrow v'' = 1$ and the $v' \leftarrow v'' = 0$ transitions allow the calculation of the separation energy $\Delta E''_{1/2}$ between the two lowest vibrational levels of the electronic ground state of the complex. The average overall observed values is $\Delta E''_{1/2} = 53.2$ cm^{-1}. Since $\Delta E''_{1/2} = \omega_e'' - 2\omega_e\chi_e''$, this is a measure of the ground-state vibrational frequency ω_e''.

C. $(1)^2\Pi \leftarrow X^2\Sigma^+$ and $(2)^2\Sigma^+ \leftarrow X^2\Sigma^+$ Bands. Figure 3 shows the experimental photodissociation spectrum in the laser energy region 16 210−17 550 cm^{-1}, which is near the atomic forbidden $4^2D_{3/2,5/2} \leftarrow 5^2S$ transition. Measurements have also been performed in the laser energy region 17 550−20 780 cm^{-1} but no photodissociation signal was recorded. In Figure 3, a band structure appears over a background, while several of the lines observed, particularly at the high-energy end of the spectrum, exhibit additional structure (not fully resolved). Without additional information, the assignment of this spectrum

TABLE 2: Spectroscopic Constants and Dissociation Energies for the Low-Lying Electronic States of Sr^+CO_2 Complex[a]

	$X^2\Sigma^+_{1/2}$	$(1)^2\Pi_{1/2}$	$(1)^2\Pi_{3/2}$	$(2)^2\Sigma_{1/2}$	$(2)^2\Pi_{1/2}$	$(2)^2\Pi_{3/2}$
ν_{00}		≤16 534	≤16 639	≤16 754	21 233	21 700
vertical excitation energy[b]		17 300	17 300	17 100	22 200	22 200
ω_e	~53	≥212	≥200	≥88	185.4 ± 2	185.9 ± 2
$\omega_e\chi_e$		8.3	7.8	1.3	0.8 ± 0.6	0.9 ± 0.2
Δ_{so}[c]		105	105		467	467
D_0 (BS)[d]	3500	≥1256	≥1190	≥1445	10 648	9507
D_0[e]		≥1522	≥1697	≥1582	5982	6317
$E_{ES}(R_e, q)$[f]	≥2645				≤7565	≤7565
ΔR_e (Å)					−0.15	−0.1
ν_{atom}[g]		14 555.9	14 836.2		23 715.2	24 516.6

[a] All values are given in reciprocal centimeters. [b] Reference 15. [c] Molecular spin−orbit splitting. [d] BS approximation. [e] Suggested values. [f] Electrostatic model, eq 3. [g] Reference 16.

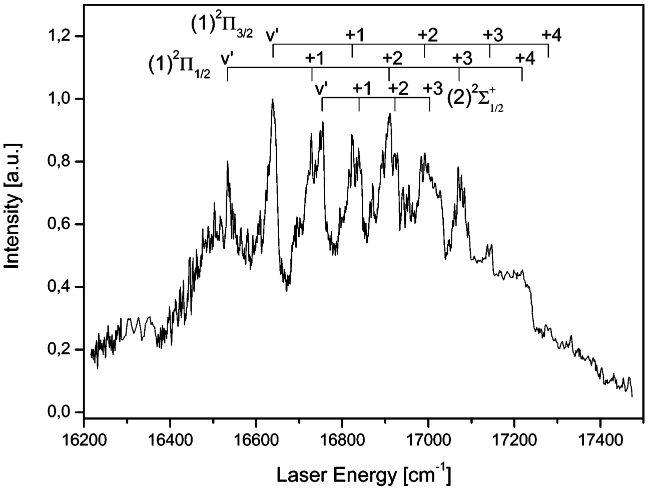

Figure 3. Photodissociation spectrum of Sr^+CO_2 corresponding to $(1)^2\Pi \leftarrow X^2\Sigma^+$ and $(2)^2\Sigma^+ \leftarrow X^2\Sigma^+$ transitions.

is complicated. According to Figure 1 the expected molecular states in this energy region are $(1)^2\Delta$, $(1)^2\Pi$, and $(2)^2\Sigma^+$.

Electronic spectra corresponding to the atomic forbidden $^2D \leftarrow {}^2S$ transition have not been observed in diatomic Sr^+−noble gas systems.[9−12] In contrast, they have been observed in Ca^+-Ne,[17] Ar, Kr,[18] and in some larger systems such as Sr^+CO,[13,14] Sr^+N_2,[19] Sr^+H_2O,[20] Sr^+NH_3,[21] Sr^+CH_3OH,[22] Ca^+Ar_2,[23] Ca^+-C_2H_2,[24] and Ca^+H_2CO.[25] In the case of Sr^+CO,[13,14] with the aid of ab initio calculations we attributed these transitions to $(1)^2\Pi \leftarrow X^2\Sigma^+$ and $(2)^2\Sigma^+ \leftarrow X^2\Sigma^+$. The calculations of Sodupe et al.[15] for Sr^+CO_2 predict a significant transition moment for both transitions, while $(1)^2\Delta \leftarrow X^2\Sigma^+$ is forbidden for a linear system.

Thus, the spectrum in Figure 3 can be attributed to electronic transitions such as $(1)^2\Pi \leftarrow X^2\Sigma^+$ and/or $(2)^2\Sigma^+ \leftarrow X^2\Sigma^+$. Which transitions are manifested by the spectrum is not straightforward to answer. In addition, several effects, such as spin−orbit and Renner-Teller splitting of the $^2\Pi$ states, can contribute to the complexity of the spectrum. The multiples in the vibrational lines suggest rather that both transitions $(1)^2\Pi \leftarrow X^2\Sigma^+$ and/or $(2)^2\Sigma^+ \leftarrow X^2\Sigma^+$ are present. The broad spectrum can also be due to these overlapping transitions.

On the basis of these considerations, we tentatively attribute the spectrum in Figure 3 to three vibrational progressions: $(1)^2\Pi_{1/2} \leftarrow X^2\Sigma^+_{1/2}$ starting at 16 534 cm^{-1}, $(1)^2\Pi_{3/2} \leftarrow X^2\Sigma^+_{1/2}$ starting at 16 639 cm^{-1}, and $(2)^2\Sigma^+_{1/2} \leftarrow X^2\Sigma^+_{1/2}$ starting at 16 754 cm^{-1}. The positions of the lines are listed in Table 3. In contrast to the spectrum in Figure 2, here the bands are blue-shifted with respect to the Sr^+ transition energy (≈14 724 cm^{-1}), indicating that the binding energies of these states are lower than that of the ground state.

TABLE 3: Positions and Assignments of the Observed $(1)^2\Pi$, $(2)^2\Sigma \leftarrow X^2\Sigma^+$ Transitions[a]

	$(1)^2\Pi_{1/2}$	$(1)^2\Pi_{3/2}$	$(2)^2\Sigma^+_{1/2}$
v'	16 534	16 640	16 754
$v' + 1$	16 728	16 823	16 839
$v' + 2$	16 910	16 993	16 922
$v' + 3$	17 071	17 145	17 003

[a] Positions are given in reciprocal centimeters.

On the basis of this assignment for the electronic states, we obtain a spin−orbit splitting of 105 cm^{-1} between the molecular $(1)^2\Pi_{1/2,3/2}$ states, which is very close to 112 cm^{-1} = $2A_D/5$, expected for a linear complex. The absolute vibrational numbering in the spectrum shown in Figure 3 is not possible, but by assuming that the first observed line in each band is $v' = 0$ and applying the same procedure as in the case of $(2)^2\Pi \leftarrow X^2\Sigma^+$ spectrum, we can obtain the spectroscopic constants $\omega_e\chi_e'$, ω_e' (lower bound), and ν_{00} (upper bound) for the three $(1)^2\Pi_{1/2}$, $(1)^2\Pi_{3/2}$, and $(2)^2\Sigma^+_{1/2}$ states. The so-obtained values are listed in Table 2.

D. Dissociation Energies. In cases in which the observed vibrational structure covers large parts of the potential well depth, the dissociation energy D_0 is given by $D_0 = \Sigma\Delta E(v)$. In the framework of the Birge−Sponer (BS) approximation,[26] which assumes a linear dependency of the vibrational spacing $\Delta E(v) = E(v + 1) - E(v)$ on v (see eq 1), the binding energy is given by $D_e = \omega_e^2/4\omega_e\chi_e$. From this the dissociation energy $D_0 = D_e - \omega_e/2 + \omega_e\chi_e/4$ is obtained.

For the $(2)^2\Pi \leftarrow X^2\Sigma^+$ spectrum the results are $D_0[(2)^2\Pi_{1/2}] = 10\,648$ cm^{-1} and $D_0[(2)^2\Pi_{3/2}] = 9507$ cm^{-1}. For the $(1)^2\Pi \leftarrow X^2\Sigma^+$ and $(2)^2\Sigma^+ \leftarrow X^2\Sigma^+$ spectrum, where an absolute vibrational assignment is not possible, we obtain in a similar manner $D_0[(1)^2\Pi_{1/2}] \geq 1256$ cm^{-1}, $D_0[(1)^2\Pi_{3/2}] \geq 1190$ cm^{-1}, and $D_0[(2)^2\Sigma^+_{1/2}] \geq 1445$ cm^{-1}.

These values are very critically dependent on the value of anharmonicity $\omega_e\chi_e$. Small changes in this parameter result in large variations in the binding energy. Furthermore, since only a few vibrational levels with low quantum numbers are observed in our spectra, an extrapolation to very high vibrational levels, which gives the limit of the binding energy (BS approximation), fails to give reasonable values.

The ab initio results of Sodupe et al.[15] show a linear Sr^+−OCO complex with a ground-state binding energy of 3500 cm^{-1} and Sr^+−C bond strength of 3.79 Å. Furthermore, they calculated the vertical excitation energies to the low-lying unperturbed electronic states (the spin−orbit splitting of the excited states has not been taken into account). These calculations allow some comparisons with our experimental results. For the $(2)^2\Pi$ states they give a value of 22 200 cm^{-1}, which is very close to the experimental value [21 700 cm^{-1} for $(2)^2\Pi_{3/2}$]; for the $(1)^2\Pi$ states the vertical energy is 17 300 cm^{-1}

(experiment 16 534 cm^{-1}); and for $(2)^2\Sigma^+$ the theoretical value is 17 100cm^{-1} (experiment 16 754 cm^{-1}). Moreover, they calculated the $5^2P \leftarrow 5^2S$ and $4^2D \leftarrow 5^2S$ excitation energies of Sr^+. For the Sr^+ ^2P state the theoretical value is 24 316 cm^{-1}, which is about 66 cm^{-1} higher than the experimental value[16] 24 250 $cm^{-1} = \nu(^2P_{3/2}) - A_P/3$ (center-of-gravity). For the Sr^+ ^2D state the energy is 14 700 cm^{-1}, that is, 24 cm^{-1} lower than the experimental value 14 724 $cm^{-1} = \nu(^2D_{5/2}) - 2A_D/5$.

These comparisons indicate the very good agreement between theoretical results and experimental ones. For this reason, we consider the theoretical value for the ground-state binding energy $D_e'' \approx D_0'' = 3500$ cm^{-1} of Sodupe et al.[15] as reliable. Furthermore, knowing the band origins ν_{00} and the atomic transitions ν_{atom} (see Table 2), we can apply the energy cycle

$$D_0' = \nu_{atom} - \nu_{00} + D_0'' \tag{2}$$

to obtain the dissociation energy D_0' of the electronic excited states, since, as mentioned above, the BS approximation does not give accurate results for D_0' in the current case. So we get for the excited states $D_0[(2)^2\Pi_{1/2}] = 5982$ cm^{-1}, $D_0[(2)^2\Pi_{3/2}] = 6317$ cm^{-1}, $D_0[(1)^2\Pi_{1/2}] \geq 1522$ cm^{-1}, $D_0[(1)^2\Pi_{3/2}] \geq 1697$ cm^{-1}, and $D_0[(2)^2\Sigma^+_{1/2}] \geq 1582$ cm^{-1}. We consider these values (listed in Table 2) as the most reasonable for the dissociation energies of the excited states of Sr^+CO_2 complex

Assuming that an intermolecular Morse potential describes the stretching mode of the pseudodiatomic Sr^+CO_2 molecule, Franck−Condon factors of the $v' \leftarrow v'' = 0$, 1 vibrational progressions are calculated in order to determine the equilibrium distance shifts ΔR_e between the $(2)^2\Pi_{1/2,3/2}$ states and the ground state. Best agreement is achieved by using the spectroscopic parameters listed in Table 2, a vibrational temperature $T = 90$ K for the ground state, $\Delta R_e = -0.15$ Å for $(2)^2\Pi_{1/2}$, and $\Delta R_e = -0.1$ Å for $(2)^2\Pi_{3/2}$.

Discussion

Assuming that the principal interaction between a metal ion and an atom or a molecule is electrostatic, then the interaction energy as a function of the internuclear distance R has the form

$$E_{ES}(R, q) = -q^2\alpha/2R^4 + q\Theta/R^3 - q\mu/R^2 \tag{3}$$

The first term describes the charge-induced dipole forces, the second one accounts for the charge−quadrupole forces, and the third term for the charge−permanent dipole forces. q is the effective charge residing in the metal ion, while the electrical properties of the molecule are described by the electric dipole polarizability α, the permanent quadrupole moment Θ, and the permanent electric dipole moment μ (in the case of polar molecules).

We can calculate the electrostatic energy in the vicinity of the equilibrium distance of the $Sr^+{-}OCO$ complex by using the theoretical[15] value R_e =3.79 Å and the experimental values[16] $\alpha = 2.6$ Å^3 and $\Theta = -3.2$ au for CO_2. The effective charge q depends mainly on the electronic state considered and varies between $q = +1e$ and $q = +2e$.[11] In the excited states correlating to the metal p orbital, which is oriented perpendicular to the internuclear axis, the molecule experiences an electrostatic attraction caused by a nearly unshielded ion core ($q \sim 2.0$). However, in the ground state the s orbital of the ion shields the core more efficiently and the charge is expected to be closer to 1.0. With these considerations we obtain for the ground state an interaction energy $E_{ES}(R_e = 3.79$ Å$, q \geq 1) \geq 2645$ cm^{-1} and for the excited state $(2)^2\Pi$ $E_{ES}(R_e = 3.665$ Å$, q \leq 2) \leq 7565$ cm^{-1}.

TABLE 4: Experimental Dissociation Energies for the Ground and Excited States, Which Correlate with the Sr^+ p Orbital for $Sr^+{-}X$ Systems

$Sr^+{-}X$	α (Å^3)	Θ (au)	μ (D)	$X^2\Sigma^+$ D_0''	$(2)^2\Pi$ D_0'
$Sr^+{-}Ne$[b]	0.4			67	595
$Sr^+{-}Ar$[c]	1.64			803	2440
$Sr^+{-}Kr$[d]	2.48			1205	2992
$Sr^+{-}Xe$[e]	4.04			1947	4116
$Sr^+{-}CO_2$	2.6	−3.2		3500	6150
$Sr^+{-}CO$[f]	1.95	−1.5	0.11	1700	6200
$Sr^+{-}H_2O$[g]	1.45	1.96	1.85	7840 ($^2A_1$)	10 465 ($^2B_2$)
$Sr^+{-}NH_3$[g]	2.22	−2.42	1.47	8540 ($^2A_1$)	11 690 ($^2A'$)

[a] Experimental dissociation energies are given in reciprocal centimeters. α is the static dipole polarizability, Θ is the permanent quadrupole moment, and μ is the permanent electric dipole moment of molecule X. [b] Reference 9. [c] Reference 10. [d] Reference 11. [e] Reference 12. [f] Reference 13. [g] Reference 27.

The binding energies for the states $(1)^2\Pi$ and $(2)^2\Sigma^+$ that correlate to the atomic 4d orbital—although not accurately determined—are lower than those correlating to the atomic 5p orbital. This is a consequence of the morphology of the Sr^+ d orbital and its orientation with respect to the intermolecular Sr^+-CO_2 axis. In this case, significant electron density exists on the molecular axis and therefore the binding will be similar to that of the ground state. With this argument one may expect stronger bonding in the $(1)^2\Pi$ state than in $(2)^2\Sigma^+$, since in the latter case (d_{z^2} orbital) significant electron density lies in the molecular axis. In contrast to this expectation, our results give similar binding energies for the $(2)^2\Sigma^+$ and $(1)^2\Pi$ states (see Table 2). This disagreement arises probably from the fact that the $(2)^2\Sigma^+$ state is also influenced from the 5p orbital. Indeed, the theoretical results from Sodupe et al.[15] show a mixing of 30% 5p and 70% 4d orbitals of Sr^+ for this state. This results in a stronger interaction than expected for a pure d_{z^2} orbital. Significant 4d/5p mixing is also observed in photodissociation spectra of Sr^+CH_3OH as reported from Qian et al.[22]

Application of the electrostatic model gives interaction energies that are very close to the dissociation energies estimated from spectroscopy. This result supports the assumption that it is electrostatic forces that primarily are responsible for the binding between a metal ion and a molecule. Further support is provided from the correlations between the dissociation energy and the electrical properties for several atoms and molecules interacting with Sr^+, which are shown in Table 4. In the last two columns the dissociation energies for the molecular states derived from 5s and 5p orbitals of Sr^+ are listed.

In the diatomic systems the dissociation energies for both ground and excited states correlate very well with the atomic polarizability and becomes stronger as α increases. In Sr^+CO_2 the negative quadrupole moment of CO_2 gives rise to charge−quadrupole forces resulting in a much stronger binding energy than that of Sr^+−noble gas complexes. Furthermore, the O atoms in CO_2 molecule are negatively charged with respect to the center (C atom) and this situation favors a linear configuration, $Sr^+{-}OCO$.

The other molecules listed in Table 4 possess a permanent electric dipole moment, and therefore an enhanced interaction is expected. In the case of Sr^+CO, the theoretical calculations of Farantos et al.[13] have shown that there are two isomers with different ground-state dissociation energies, $Sr^+{-}CO$ ($D_0'' \approx 1200$ cm^{-1}) and $Sr^+{-}OC$ ($D_0'' \approx 1700$ cm^{-1}). We consider the Sr^+OC complex, and by use of eq 2 we obtain the dissociation energy $D_0' \approx 6200$ cm^{-1} for the excited $(2)^2\Pi$ state. Thus, the binding in $Sr^+{-}CO$ is similar to that of $Sr^+{-}CO_2$

because the dipole moment of CO is not very large and the charge−permanent dipole forces contribute only about 10% in the total interaction.

For Sr^+ interacting with the polar molecules H_2O and NH_3, there are theoretical calculations from Sodupe and Bauschlicher[27] about the structure and binding. In the bottom of Table 4 we list the dissociation energies of the Sr^+H_2O and Sr^+NH_3 systems, which in the ground state exhibit C_{2v} and C_{3v} symmetry, respectively, and therefore the excited states derived from the 5p orbital are termed as $^2B_1$ and $^2A'$. The large dipole moment of both molecules causes very strong binding to Sr^+ in comparison to Sr^+-CO_2.

Finally, the dissociation energy of Mg^+CO_2[28] is larger than that of Sr^+CO_2 in the ground state ($D_0'' = 5150$ cm^{-1}) and in the excited ($D_0' = 11\,194$ cm^{-1}) state. This is expected from eq 3 because Mg^+ has a smaller ionic radius, allowing a closer approach of the CO_2 molecule.[15]

Conclusions

In this paper we have examined the photodissociation spectroscopy of mass-selected Sr^+CO_2 complex. We have recorded spectra in the laser energy region 16 210−22 990 cm^{-1}. In the region 20 780−22 990 cm^{-1}, the spectrum consists of two vibrational progressions, which correspond to dipole transitions from the $X^2\Sigma^+_{1/2}$ ground state to the excited $(2)^2\Pi_{1/2}$ and $(2)^2\Pi_{3/2}$ states. The spin−orbit splitting of these bands suggests a linear Sr^+-OCO complex, in agreement with ab initio calculations. In the 16 210−17 550 cm^{-1} laser energy region, a broad spectrum consisting of some vibrational progressions is recorded. With the aid of ab initio calculations of Sodupe et al.,[15] we have assigned these progressions to $(1)^2\Pi_{1/2} \leftarrow X^2\Sigma^+_{1/2}$, $(1)^2\Pi_{3/2} \leftarrow X^2\Sigma^+_{1/2}$, and $(2)^2\Sigma^+_{1/2} \leftarrow X^2\Sigma^+_{1/2}$ transitions. Also in this case the observed spin−orbit splitting for $(1)^2\Pi_{1/2,3/2}$ indicates a linear complex. By use of the spectroscopic constants of the investigated states, we could estimate the dissociation energies. Finally, we have discussed the results obtained in the framework of electrostatic interactions, and comparisons with similar systems have been made.

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