Photofragmentation spectra of Sr^+CO complex: experiment and ab initio calculations

S.C. Farantos [a,b,*], E. Filippou [a,b], S. Stamatiadis [a], G.E. Froudakis [b], M. Mühlhäuser [c], M. Massaouti [a,b], A. Sfounis [a,b], M. Velegrakis [a]

[a] *Institute of Electronic Structure and Laser, Foundation for Research and Technology, Hellas, Iraklion, Crete 71110, Greece*
[b] *Department of Chemistry, University of Crete, Iraklion 71110, Crete, Greece*
[c] *Institut für Physikalische und Theoretische Chemie der Universität Bonn, Wegelerstrasse 12, 53115 Bonn, Germany*

Abstract

The optical absorption spectrum of Sr^+CO is measured by photofragmentation spectroscopy of mass selected ions. The spectrum, in the energy interval of 19 000–23 000 cm^{-1}, shows a regular vibrational structure with peaks separated by approximately 200 cm^{-1}, plus a low intensity shoulder which covers an energy range up to the dissociation. Electronic configuration interaction calculations reveal the existence of a bistable species with strontium either bonded to the carbon-end or to the oxygen-end of CO in collinear geometries. The assumption that the spectrum depicts excitations from both isomers is examined.
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1. Introduction

Small molecules interacting with metal cations apart from their own interest serve as prototype systems for understanding the structure and bonding in larger molecules. Cations of alkali and alkaline earths have extensively been studied because of their importance in biology [1]. Duncan and collaborators investigated complexes of Mg^+ and Ca^+ with CO_2, H_2O and N_2 [2]. Prior to this work, Bauschlicher et al. [3] had carried out extensive ab initio electronic structure calculations for a variety of metal cations with inert gases and molecules. Among them they studied Mg^+ interacting with CO_2 and N_2 [4,5] as well as Sr^+ with CO_2 [4].

Recently, in a series of three articles [6–8] we have investigated the mass selected photofragmentation spectra of positively charged strontium with argon atoms. Clusters with up to eight argon atoms were studied. Combining ab initio configuration interaction calculations [6] with semiempirical potentials and classical molecular dynamics we have successfully simulated the photofragmentation spectra [7,8]. The interactions are found to be mainly electrostatic for the ground electronic state in accord to other studies which involve molecules, such as Sr^+CO_2 [4].

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* Corresponding author. Fax: +30-81-39-1305.
  E-mail address: farantos@iesl.forth.gr (S.C. Farantos).

Alkali cations interacting with carbon monoxide have also been investigated by first principle electronic structure calculations [9], the results of which were used to interpret the IR spectra of basic zeolites, after the low-temperature absorption of CO. Apart to the main band, which is due to the carbon-bonded isomer, a second weak band was observed and it was attributed to the oxygen-bonded alkali metal cation to CO.

In this Letter we report the photofragmentation spectra of Sr^+CO. The complex is selected from a cluster distribution, $Sr^+(CO)_n$, produced in a molecular beam apparatus. Usually, carbon monoxide is used as a probe species in vibrational spectroscopy because of its frequency shift due to the bonding [9]. However, the kind of spectroscopy we have applied is based on the electronic excitations of Sr^+, in an energy range of 15 000–23 000 cm^{-1}. The excited states of CO are considerably higher in energy. Thus, mass selected photodissociation spectra allow for the observation of isolated complexes. To elucidate the characteristic spectra of Sr^+CO we have carried out electronic configuration interaction calculations for all states involved in the photofragmentation spectroscopy. The ab initio points are fitted by B-splines to produce analytical representations of the potential energy surfaces (PES), which are then used to solve the time dependent Schrödinger equation and to simulate the vibrational spectra in the pertinent electronic states. By comparing theoretical and experimental results the assumption for the existence of a bistable species with two linear isomers, the C-bonded and the O-bonded Sr^+ to CO, is investigated.

2. Results and discussion

The $Sr^+(CO)_n$ clusters are formed in a molecular beam apparatus via the injection of a plasma plume produced by the laser (Nd:YAG at 1064 nm) ablation of a Sr target, into a supersonic expansion of CO gas into vacuum. The cationic complexes produced are accelerated by a pulsed double field time of flight (TOF) device towards a reflectron assembly. The backwards 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 ions are selected through a mass gate from the whole cluster size distribution. Shortly behind the mass gate 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. If photofragmentation occurs, the parent and the fragments are separated in the TOF spectrum because of the reflectron. The photofragmentation spectrum is obtained by measuring the intensity ratio of the ionic fragments to the total signal and normalized by the laser intensity. Assuming that each absorbed photon leads at least to one fragmentation event in the time window of the measurement (10 μs), then the measured photofragmentation cross-section is equal or constitutes a lower limit for the photoabsorption cross-section.

Sr^+ in its ground electronic state has one electron in the 5s orbital, hence a $^2\Sigma$ state for Sr^+CO. The first excited atomic states are the 4^2D, 5^2P and 6^2S. Absorptions are recorded in the energy ranges of 15 600–16 100 cm^{-1} and they are attributed to states originated from the 4^2D state of strontium. In $C_{\infty v}$ symmetry the five D degenerate states are split into $^2\Sigma$, $^2\Pi$ and $^2\Delta$. The higher energy bands between 19 000 and 23 000 cm^{-1} are due to excitations of the 5^2P states of strontium, $^2\Sigma$ and $^2\Pi$. These two spectra are remarkably different, although both show two bands with some vibrational structure. The low energy spectrum consists of broad overlapping peaks spanning an energy interval of 500 cm^{-1}. The high energy spectrum shows sharp regular progressions in an energy range of 4000 cm^{-1}. The most characteristic feature of this spectrum is a low intensity shoulder spanning an energy range of 2000 cm^{-1}. The elucidation of this spectrum is the theme of the present Letter leaving for a future publication the discussion of the spectrum associated with the 4^2D states of strontium [10].

In Fig. 1a the total photodissociation spectrum of Sr^+CO complex is depicted. This is the result from excitations to the $2^2\Pi$ state originating from the 5^2P states of strontium. We have subtracted from all lines 19 000 cm^{-1} to compare with the
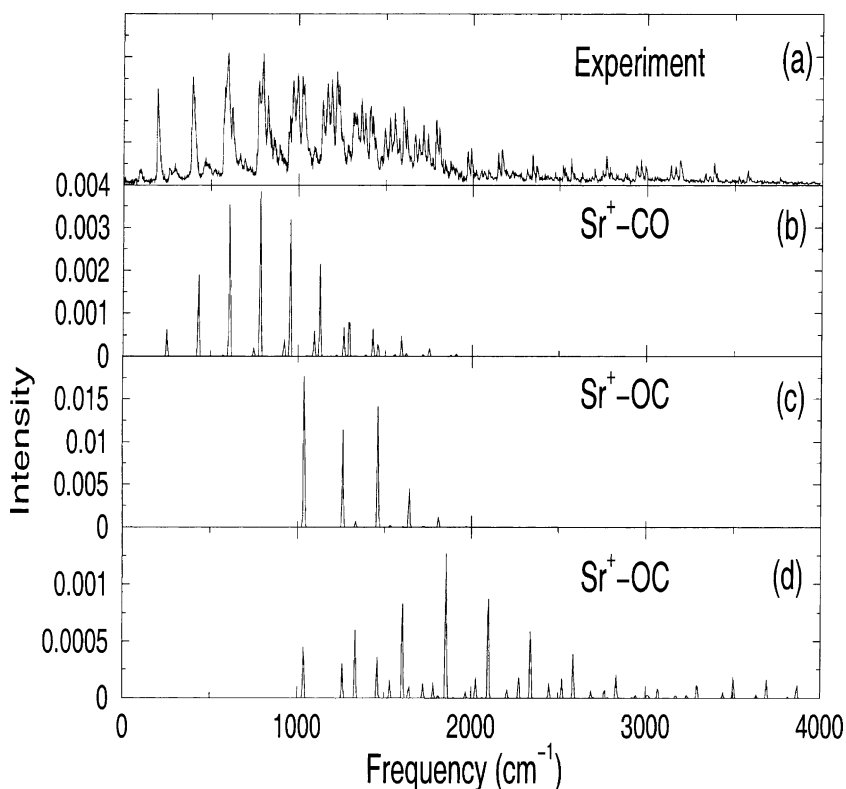
Fig. 1. (a) Experimental spectrum in the range of $19\,000$–$23\,000$ cm^{-1}. (b) Calculated spectrum in $3^2A''$ state with an initial Gaussian wave packet centered at Sr$^+$–CO minimum of the ground electronic state. (c) Spectrum produced with an initial Gaussian wave packet centered at the minimum of Sr$^+$–OC. (d) Similar as that of c but with an initial Gaussian wave packet broaden in the angle coordinate. See text.

theoretical spectrum later on. Peaks about every 200 cm^{-1} appear. There is a low intensity part, which looks like a continuation of the high intensity peaks with clumps of lines approximately separated by 200 cm^{-1}. However, we can see multiple lines even after the third peak. For a system such as Sr$^+$CO several phenomena contribute to the complexity of the spectrum. The spin-orbit splitting of the $^2\Pi$ state is estimated to be about 500 cm^{-1}, which approximately corresponds to the third peak in Fig. 1a. Another phenomenon which makes the spectra to appear more congested is the Renner–Teller; i.e., the twofold degeneracy of the Π state for linear configurations of the nuclei is lifted at geometries in the plane and two separate adiabatic potential energy surfaces dictate the dynamics of the complex. In C$_s$ symmetry the two states give A$'$ and A$''$

irreducible representations, respectively. To find out the morphologies of these PESs electronic structure calculations are required. Finally, although we can not determine the temperature of the initial clusters some hot bands are expected and these could explain the small peaks that appear among the main ones in Fig. 1a.

The computations of the electronically excited states were performed with the multi-reference single- and double-excitation configuration interaction method, MR-CI, implemented in the MOLPRO 2000 package of programs [11]. Moreover, the geometry of Sr$^+$CO in the ground electronic state has been fully optimized using spin-restricted singles and doubles coupled cluster calculations with a perturbative inclusion of the connected triple excitations RCCSD(T). For carbon and oxygen we used the correlation-consistent

triple zeta basis set of Dunning [12] augmented by two d- and one f-polarization functions. The exponents taken are $4d(C) = 1.09, 0.31, 4d(O) = 2.314, 0.645, 5f(C) = 0.76, 5f(O) = 1.428$. For strontium atom we used a quasi-relativistic effective core potential (ECP) from the Stuttgart group [13] in conjunction with the correlation-consistent triple zeta basis set of Dunning [12].

Preliminary calculations employing a smaller polarized basis set for strontium, i.e., expanding the cc-p-VTZ basis by only one f-function, cc-p-VTZ+(f), with an exponent of $\alpha_f(Sr) = 7.09$ (again optimized in an atomic calculation) show almost no changes in excitation energies and transition probabilities of the excited states examined in this work. Furthermore, calculations showed that enlarging this basis by Rydberg functions or by employing more functions in the polarization and correlation description changed the results for the transition energies generally by less than 0.1 eV.

The chosen basis set is flexible with respect to polarization and electronic correlation and is considered to be fairly balanced for all states treated. For the calculation of the equilibrium geometry (RCCSD(T)) the basis set was enlarged by two f-functions and one g-function located at the strontium center (cc-p-VTZ+(2f,g)). The exponents taken are $5f(Sr) = 0.984, 5f(Sr) = 0.492$ and $6g(Sr) = 0.738$. They have been optimized for the Sr^+ atom. The contribution of higher excitations is estimated by applying a generalized Langhoff–Davidson correction formula

$$E(MRD - CI + Q) = E(MRD - CI) - (1 - c02)$$
$$\times [E(ref.) - E(MRD - CI)]$$
$$/c02, \qquad (1)$$

where $c02$ is the sum of squared coefficients of the reference species in the total CI wavefunction and $E(ref.)$ is the energy of the reference configurations.

Fig. 2a exhibits the potential energy curves for strontium coaxially approaching the carbon-end of CO. Eight states are shown in $C_{\infty v}$ symmetry although only the first five are related to the recorded spectra. Similarly, Fig. 2b shows the potential curves for Sr^+ approaching the oxygen-end of CO. In Table 1 we tabulate the equilibrium
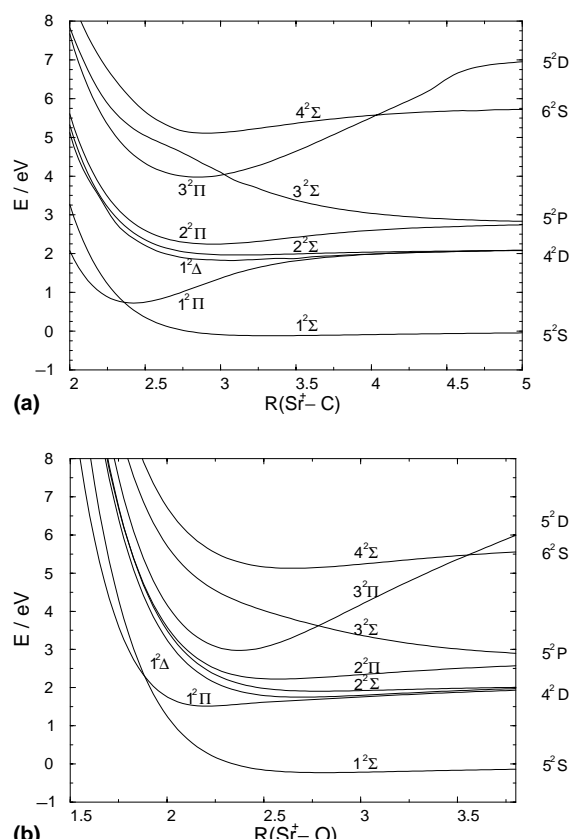

Fig. 2. (a) Potential energy curves for Sr^+ coaxially approaching the carbon atom. (b) Potential energy curves for Sr^+ coaxially approaching the oxygen atom. The zero of energy is defined for the dissociation limit, $Sr^+(5^2S) + CO(X^2\Sigma^+)$.

bond lengths, binding energies, vertical transitions and dissociation limits for the carbon-bonded isomer, and in Table 2 the corresponding data for the oxygen-bonded isomer. All energies are measured with respect to the dissociation limit of the ground electronic state, $Sr^+(5^2S) + CO(^1\Sigma^+)$, for which the zero energy is defined.

To evaluate the accuracy of the basis sets used, we compare at the dissociation limit the excited states of Sr^+ with the experimental values [14], and we find a difference of 0.3 eV for the 4^2D state and 0.1 eV for the 5^2P state. The calculations reveal linear absolute and relative minima for all states except the repulsive $3^2\Sigma^+$. In the ground electronic state the binding energies are 0.15 and 0.21 eV for the carbon-bonded and oxygen-bonded isomer,

Table 1
Strontium–carbon equilibrium bond lengths (r_e), binding energies (E_b), vertical transitions (T_e) and dissociation energies (E_d) for Sr$^+$–CO

State	r_e	E_b	T_e	E_d
$1^2\Sigma^+$	3.31	0.149	–	0
$1^2\Pi$	2.42	1.510	1.781	2.146 (1.805 $4^2D_{3/2}$)[b] (1.839 $4^2D_{5/2}$)[b]
$1^2\Delta$	3.10	0.198	1.992	2.132
$2^2\Sigma^+$	3.12	0.226	2.094	2.154
$2^2\Pi$	2.96	0.666	2.423 (2.39)[a]	2.830 (2.940 $5^2P_{1/2}$)[b] (3.040 $5^2P_{3/2}$)[b]
$3^2\Sigma^+$	–	–	3.704	2.815
$4^2\Sigma^+$	2.90	0.708	5.192	5.752 (5.919 $6^2S_{1/2}$)[b]
$3^2\Pi$	2.84	3.383	4.275	7.151 (6.607 $5^2D_{3/2}$)[b] (6.617 $5^2D_{5/2}$)[b]

The zero energy corresponds to Sr$^+$(5^2S) + CO($^1\Sigma^+$) with calculated energy −143.239223 Hartree. Energies are in eV and distances in Å. The distance of CO was kept fixed at 1.201 Å. The numbers in parentheses are experimental results.

[a] The first intense peak in the spectrum of Fig. 1a.

[b] Excitation energies of Sr$^+$ from [14].

Table 2
Strontium–oxygen equilibrium bond lengths (r_e), binding energies (E_b) and vertical transitions (T_e) for Sr$^+$–OC

State	r_e	E_b	T_e
$1^2\Sigma^+$	2.81	0.214	–
$1^2\Pi$	2.21	0.621	1.928
$1^2\Delta$	2.70	0.378	1.985
$2^2\Sigma^+$	2.79	0.243	2.133
$2^2\Pi$	2.57	0.593	2.499 (2.490)[a]
$3^2\Sigma^+$	–	–	3.815
$4^2\Sigma^+$	2.65	0.601	5.382
$3^2\Pi$	2.37	4.168	3.913

Energies are in eV and distances in Å. The distance of CO was kept fixed at 1.201 Å.

[a] Estimated origin of the Sr$^+$–O stretch progression in the spectrum of Fig. 1a (see text).

correspondingly. Thus, the binding of strontium to the oxygen side results in a slightly more stable complex. On the other hand, in the $2^2\Pi$ state the binding energies are 0.67 eV for the C-bonded and 0.59 eV for the O-bonded isomer. The vertical transitions from the equilibrium geometries of both isomers in the ground electronic state to $2^2\Pi$ state are 2.42 and 2.50 eV for the relative and the absolute minima, respectively. The numbers in parentheses are the energies of the first intense peak (Table 1), and a possible origin of the Sr$^+$–OC absorption at 20 030 cm^{-1} (Table 2) in Fig. 1a. From this line a new progression starts with energy gaps that could correspond to Sr$^+$–O stretch. From the same Tables we can also see that, between the $1^2\Sigma^+$ and $2^2\Pi$ states the equilibrium bond length of Sr$^+$–C is contracted by 0.7 Å, and that of Sr$^+$–O by 0.24 Å. The bond length of CO in Sr$^+$–CO complex was found to be 1.201 Å, which is larger than the bond length of the free molecule (1.128 Å). For the O-bonded species the CO bond length at the RCCSD(T) level of theory is 1.16 Å.

To construct potential energy surfaces, in this study we take the CO bond length fixed at 1.201 Å, assuming that the high frequency CO oscillator can be adiabatically separated. Analytical representations are obtained by employing about 600 ab initio points for each state and using Jacobi coordinates; the distance of Sr$^+$ from the center of mass of CO, R, and the angle between R and the bond length of CO, γ. We have constructed nine analytical potential energy surfaces as series in a bicubic B-spline expansion. Routines from the NAG library [15] are used which combine the spline representation with a least square fit for finding the coefficients in the expansion. The root

mean square deviations are from 0.01 to 0.1 eV. In the present work, we give details for the morphologies of two states ($5^2A'$ and $3^2A''$) originated from the $2^2\Pi$ and we leave the description of the others for a future publication [10].

These two surfaces have their minima at collinear geometries. The A'' surface is lower than the A' for configurations around the minima. Their main differences occur in the area of the transition state for the isomerization of Sr^+–CO to Sr^+–OC. The similar morphology of the two adiabatic PES usually implies a weak Renner–Teller coupling.

Using these PES we have calculated vibrational spectra by solving the time dependent Schrödinger equation and employing Gaussian initial wave packets. To evaluate the action of the Hamiltonian to the wavefunction we use high order finite difference methods as described in [16]. The time propagation was performed with the Chebyshev expansion method [17].

In Figs. 1b–d we show the spectra obtained from the $3^2A''$ state. Similar results have been given by the $5^2A'$ state. The spectra are produced as the Fourier transform of the autocorrelation function of an initial Gaussian wavefunction centered at the equilibrium point of Sr^+–CO (Fig. 1b) and Sr^+–OC (Figs. 1c–d) of the ground electronic state. We follow the time evolution of the wave packets in the $3A''$ surface. The vibrational levels are measured with respect to the absolute minimum of this potential. However, to compare with the experiment we translate the lines of the Sr^+–OC isomer, such as the first peak to coincide with the experimental line at 20 030 cm^{-1}. The difference between the two spectra in Figs. 1c and d is due to the initial wave packet. The high intensity lines of Fig. 1c correspond mainly to stretch excitations, whereas the spectrum shown in Fig. 1d is produced with a Gaussian which is broadened along the angle coordinate, thus exciting bending overtones and stretch–bend combination levels.

According to our calculations, we can see, that the recorded spectrum extends almost up to the dissociation of the cluster in the $2^2\Pi$ state (≈ 4800 cm^{-1}, Table 1). The calculated spectrum of Sr^+–CO complex (Fig. 1b) consists of two progressions. The high intensity lines are the Sr^+–C stretch overtones with quantum numbers $v = 0$–6,

and the second progression is a combination of bend and stretch excitations. The energy difference of the first adjacent stretch levels is about 180 cm^{-1}, which matches with the experiment. Similarly, the excited vibrational levels of the O-bonded isomer (Fig. 1c) consist of Sr^+–O stretch levels. The energy differences of the first adjacent stretch levels are 220–202–180 cm^{-1}. The intense lines of Fig. 1d correspond to levels with mainly bend excitation. The stretch is either not excited or excited with one or two quanta. The bend vibrational levels are highly anharmonic.

Combining the spectra shown in Figs. 1b and c we could argue that the broad spectrum observed in the Sr^+–CO complex is due to the excitation of both isomers. We have found, that the barrier of isomerization in the ground electronic state is close to dissociation. Hence, we expect the isomerization rate to be rather small and both species should be formed when the clusters are initially generated. However, the poor agreement in the intensities make an unequivocal assignment difficult. The fact that we have ignored the Renner–Teller interaction, we believe, that it is not a bad approximation for the high vibrational levels, provided the nonadiabatic interaction is weak. Therefore, the accuracy of the potential energy surfaces at present is the determining step in obtaining better agreement.

3. Conclusions

A regular vibrational spectrum produced from the excitation of the $2^2\Pi$ state of Sr^+–CO complex covers almost the total energy range from the zero-point energy up to dissociation. This is consistent with the calculated potential energy surfaces which predict no crossings among them in the experimental excitation energies, thus, resulting in long living complexes. Half of the spectrum consists of progressions of low intensities. Ab initio configuration interaction calculations reveal a bistable complex with Sr^+-bonded either to the carbon or to the oxygen atom in collinear geometries. For non-linear configurations the degenerate Π state is split into an A' and an A'' state. The vibrational spectra obtained by solving the two dimensional

time dependent Schrödinger equation and initial Gaussian wavefunctions approximating the ground vibrational states of Sr^+–CO or Sr^+–OC do not cover the complete energy range found in the experiment, despite of the qualitative agreement in the positions of spectral lines. It turns out, that by allowing the excitation of the bending levels of Sr^+–OC complex part of the long tail is recovered.

Acknowledgements

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