Observation of a barrier and a double well in the potential curve of the C-state of the CO^+ molecule.

by

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Abstract

The C-state of CO^+ has been studied using UV photoelectron spectroscopy. The spectrum was excited by a monochromatized HeIIα ECR source. The vibrational progression in the C state has earlier been observed up to v=6 and an anomalous anharmonicity has been inferred. In the present spectrum the progression has been followed up to v=11 and the progression can be described as originating from two nearly harmonic potentials. A perturbation is thus found for the C state at an internuclear distance of about 1.4 Å. Moreover, the progression extends 0.2 eV above the dissociation limit and therefore a potential barrier must exist with a maximum around 2.3 Å.

The electron structure in the inner valence region of the CO molecule has been extensively studied. Different methods have been used such as classical Optical Spectroscopy [1], X-ray photoelectron spectroscopy (XPS) [2], UV photoelectron spectroscopy (UPS) [3-5], Synchrotron Radiation Photoelectron Spectroscopy (SRPS) [6] and Deexcitation Spectroscopy (DES) (also referred to as Resonance Auger Spectroscopy) [7]. A particular interest has been focussed on the electronic structure of CO since this molecule has been the subject of various surface studies related to the catalysis problem [8,9].

In a recent UPS study of the valence photoelectron spectrum of N_2, CO and O_2, using monochromatized HeII excitation, rich vibrational structure has been observed for several inner valence states. In particular, in the case of CO vibrational progressions have been found for the D,C, E, G states and possibly also for the K state [10].

The C state has been studied earlier using non-monochromatized HeII radiation [3-5] and a progression has been identified that could be associated to this state. In these spectra the vibrational structure was not completely resolved and it was difficult to determine the adiabatic binding energy. This was partly due to the overlap between the D and C states. In both these studies, five clearly resolved peaks could unambiguously be related to the C state, while two more states were inferred at lower binding energy. Potts and Williams [4] also inferred one weak line at higher binding energy that should belong to the C state progression. In a later study the data were analyzed by Codling and Potts [5]. An anomalous value of the anharmonicity constant was found and the authors connected this to the "dissociation limit at 24.34 eV for the process $CO^+ \rightarrow C^+ (^2P^o) + O^*(^1D)$". This process implies an interaction between the C $^2\Sigma^+$ state with another electronic state of the same symmetry, leading to an anomalous potential curve.

This conjecture was adopted also by Locht [11] in a study of the dissociative ionization of CO. Locht proposed that the other electronic $^2\Sigma^+$ state should be characterized by a large internuclear equilibrium distance and he also sketched a hypothetical potential curve for this state that was correlated to the $CO^+ \rightarrow C^+ (^2P^o) + O^*(^1S)$ dissociation process with a "limit at 26.6 eV".

In the present study we have recorded a high resolution photoelectron spectrum between 21.5 and 25 eV including both the D and C states in the inner valence region of CO^+, shown in Fig.1. The measurements were carried out by means of an electron spectrometer designed for gas phase studies [12]. The spectrometer was equipped with an ECR microwave UV source [13]. The HeII radiation at 40.8 eV was used, and other radiation components of the discharge were suppressed using a newly designed monochromator [14]. The sample gas was commercially obtained with a purity of 99.995%. The energies were calibrated against the He$1s_{1/2}$ line at 24.587 eV excited with HeIIα radiation.

Due to the overlap with the B-band excited with the 320 Å line, which was not entirely removed by the monochromator, it is difficult to identify the 0-0 transition of the D state (cf Fig.1). Åsbrink and Fridh [3] used a deconvolution procedure to identify this transition and found that it should coincide with the 0-1 peak at 22.039 eV of the 320 Å spec-

trum. In the present spectrum of Fig. 1 the vibrational structure is clearly resolved. As can be seen, the peak at 22.2 eV is broadened due to the fact that the energies of the overlapping lines are somewhat different. A vibrational line from the D state with lower energy would give rise to an asymmetry on the high binding energy side of the v=1 peak of the B state (320 Å). Since this is not observed we conclude that the peak at 22.2 eV corresponds to the 0-0 transition of the D state. Using curve fitting we have determined the energy of this transition to 22.204 eV. The vibrational energies for the peaks in the D state, as determined from the spectrum in Fig. 1, are given in Table 1.

It has earlier been difficult to determine the adiabatic binding energy also of the C state due to the overlapping lines of the D state. As seen in Fig.1 the structure is quite well resolved in the present spectrum, allowing identification of the adiabatic peak. See Table 1.

As seen in Fig. 1 and Table 1, the vibrational spacing of the C state is practically constant in the first part of the band as well as in the end of the progression. However, the vibrational energy differs significantly in these two separate regions, with a radical decrease occurring between v=4 and 6. The vibrational energies are plotted versus the vibrational quantum number in Fig.2. The anomalous anharmonicity observed earlier can now be seen in detail. The plot can readily be fitted to two second degree polynomials with very different vibrational energies and with a very small anharmonicity for each separate region. Thus, the conjecture made by Locht [11] can now be unambiguously confirmed and it is also possible to draw a new potential curve for the C state based on these experiments.

This curve, which is shown in Fig. 3, was obtained from two Morse potential curves were derived from the fittings shown in Fig.2. The narrowest part of the curve, corresponding to v=0-4, extends to the bottom of the potential well. By a Franck-Condon analysis of the intensities for the v=0 to v=4 lines, the internuclear equilibrium bond distance is found to be 1.25Å. The Morse curve corresponding to the broader part is obtained from the v=6-11 lines and has been given a bond distance that aligns it to the inner part of the narrower curve in the v=6-11 range. These two curves together form a double potential well which possibly contains a small barrier at the v=5 level, where the vibrational spacing starts to decrease markedly. The detailed shape of the potential curve in this region is not easily determined from the experimental data and is therefore indicated in Fig.3 with a dashed line.

It is possible to draw some conclusions about the crossing $^2\Sigma^+$ state potential curve proposed by Locht [11]. Two $^2\Sigma^+$ states must be correlated to the $C^+(^2P)+O(^1D)$ dissociation limit. Therefore, both the B state and the perturbed C state must be correlated to this dissociation limit. However, the highest observed vibrational state in the C band lies 0.2 eV above the $C^+(^2P)+O(^1D)$ dissociation limit at 24.19 eV. Thus a potential barrier must exist in the C state potential curve at about 2.3 Å internuclear distance. See Fig.3.

As a consequence one has to conclude that the C state is perturbed by two other states. The first crossing causing the perturbation around 1.4 Å probably involves the I $^2\Sigma^+$ state observed at about 31 eV in the UPS [10] and XPS [2]. This state must now be correlated

to the $O^+(^4S)+C(^3P)$ limit at 24.58 eV [15,16] and should have a potential minimum around 1.5 Å. This potential curve also crosses the F $^2\Sigma^+$ state in the vicinity of its potential minimum, as proposed by Fig.10 in ref [11]. The potential barrier for the C state around 2.3 Å implies interaction with another $^2\Sigma^+$ state. One possibility is that the J state observed at about 32 eV in the XPS [2] crosses the F state and consequently forces the latter state to dissociate to the $C^+(^2P)+O(^1S)$ dissociation limit at 26.42 eV [15,16]. See Fig. 3.

In conclusion, the use of monochromatized HeIIα for excitation of a high resolution inner valence photoelectron spectrum including the D and C states has enabled an experimental determination of the potential curve for the C state. This curve exhibits a very complex shape with two regions of strong perturbations, one at an internuclear distance of about 1.4 Å and another at about 2.3 Å. The latter corresponds to a potential barrier through which tunneling into the dissociation continuum may occur from high vibrational levels. The first perturbation gives rise to a potential curve that suddenly widens but retains its harmonic character even above the perturbation energy. Further research using monochromatized HeIIα radiation will probably reveal similar phenomena in the inner valence region of related systems.

ACKNOWLEDGEMENT

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TABLES

Table 1.

a. Vibrational energy levels for the $C^2\Sigma^+$ state in CO^+.

Vibrational quantum number, v	Binding Energy (eV)	Line Width (FWHM) (eV)	Relative Intensity
0	23,01	0,07	0,2
1	23,195	0,071	0,72
2	23,381	0,068	1,00
3	23,559	0,080	0,83
4	23,734	0,071	0,75
5	23,877	0,071	0,61
6	23,993	0,071	0,43
7	24,084	0,071	0,33
8	24,168	0,071	0,28
9	24,249	0,071	0,24
10	24,329	0,068	0,23
11	24,410	0,068	0,21

b. Vibrational energy levels for the $D^2\Pi$ state in CO^+.

Vibrational quantum number, v	Binding Energy (eV)	Line Width (FWHM) (eV)	Relative Intensity
0	22,204	0,07	0,07
1	22,380	0,07	0,3
2	22,554	0,07	0,7
3	22,726	0,07	1,0
4	22,895	0,07	1,0
5	23,062	0,08	0,7
6	23,225	0,07	0,2

FIGURES

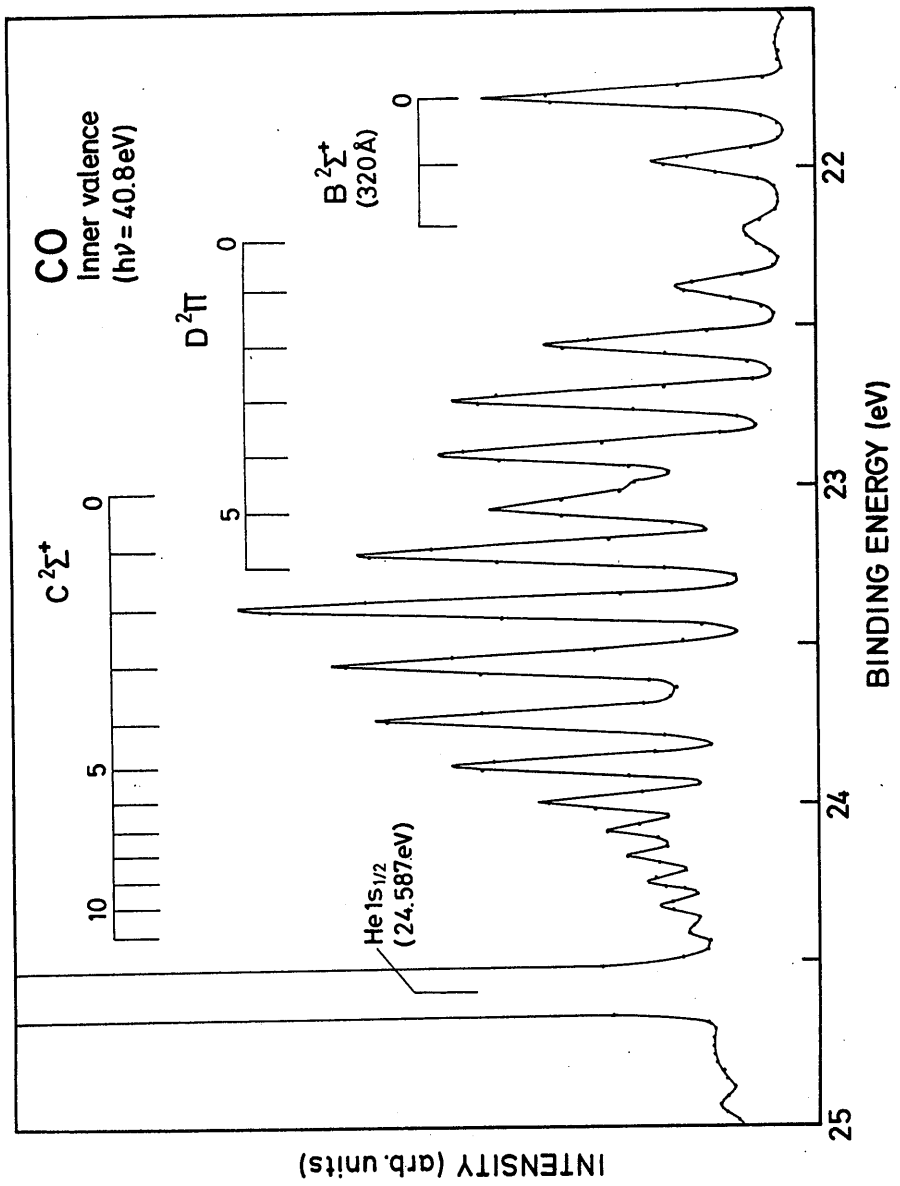

Fig.1. *A high resolution photoelectron spectrum between 21.5 and 25 eV including both the D and C states in the inner valence region of CO^{+}.*

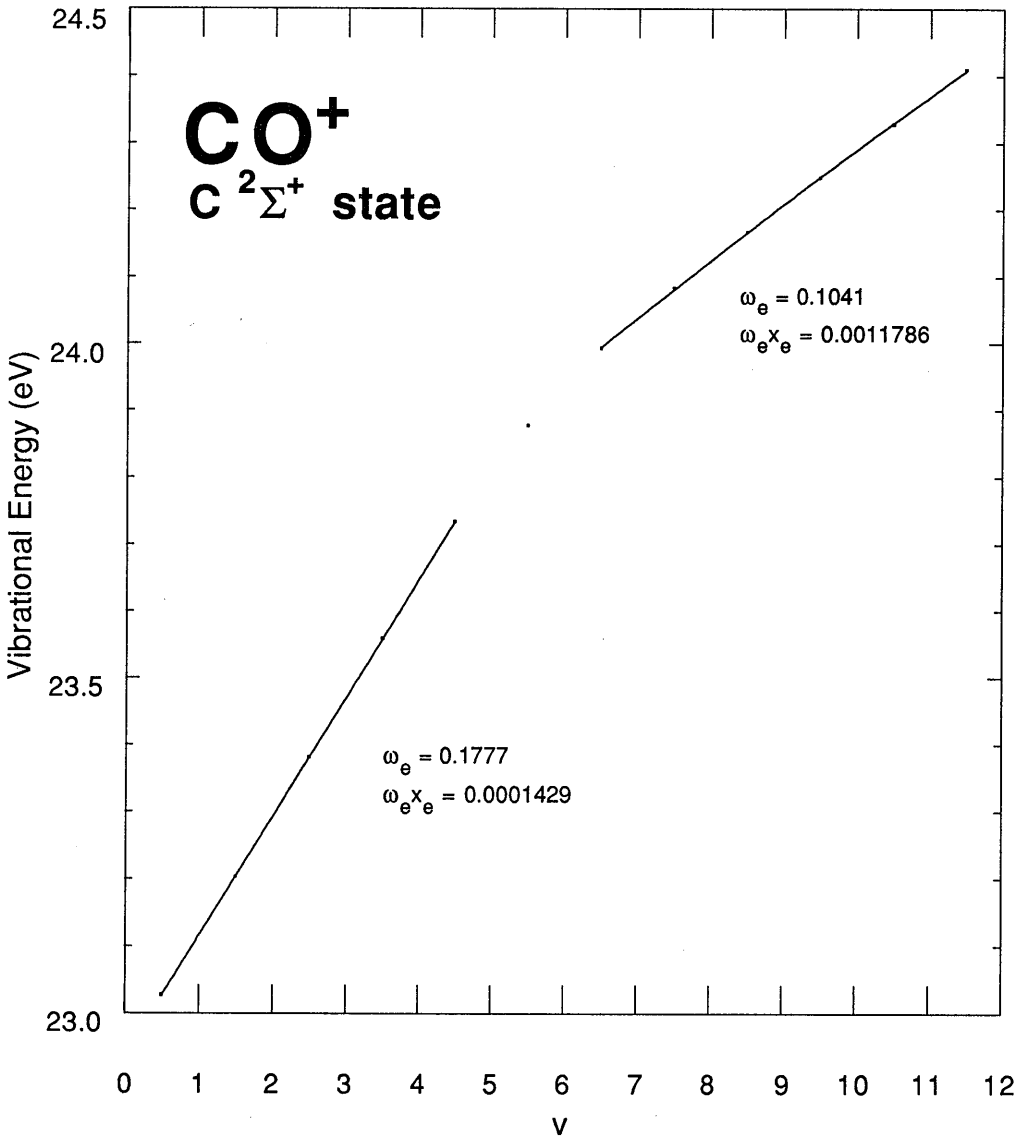

Fig.2. *The binding energies of the lines in the C state progression plotted versus the vibrational quantum number.*

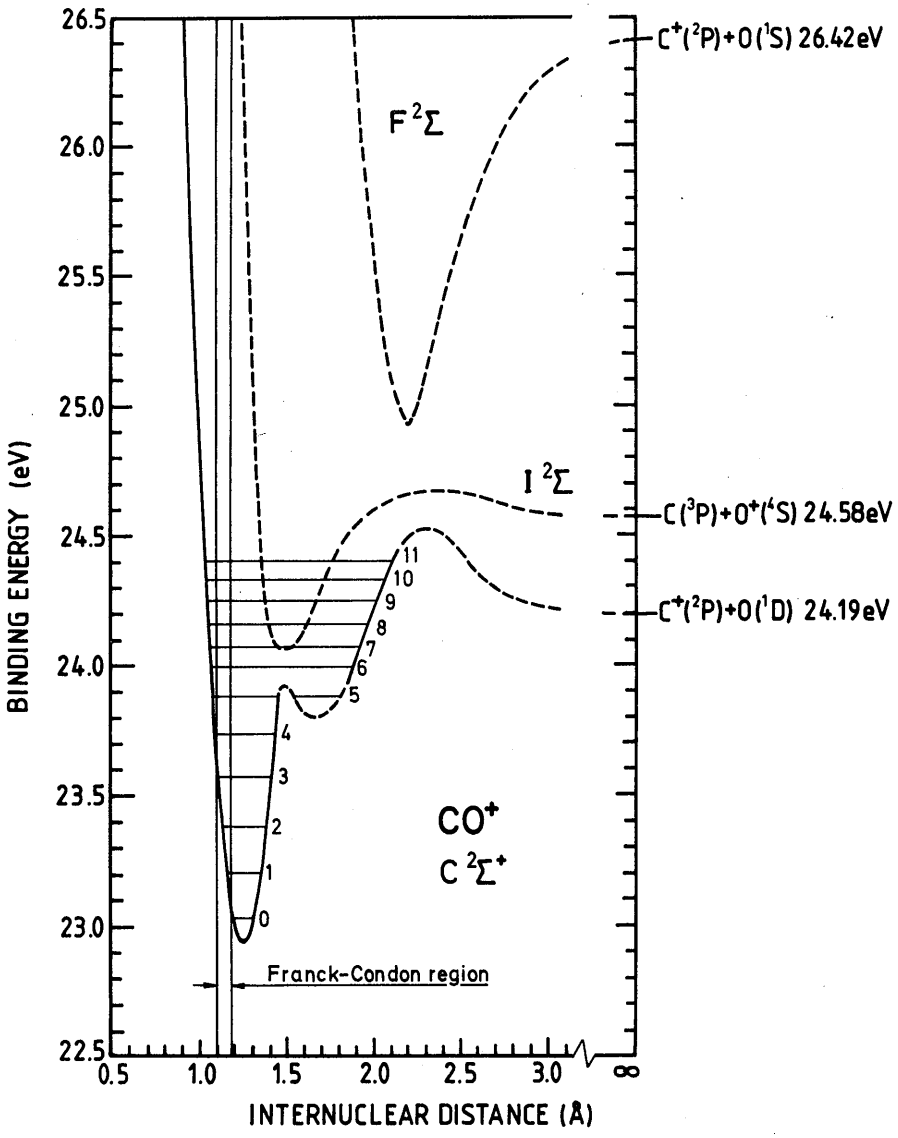

Fig.3. *The anomalous potential curve for the C state. The inferred interacting F and $I\,^2\Sigma^+$ states are indicated by dashed lines.*