THE DISSOCIATIVE IONIZATION OF CO BY ELECTRON IMPACT.
THE C⁺ ION FORMATION

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The interest of a study of the dissociative ionization of CO is twofold. (i) This molecule is isoelectronic of the N₂ molecule, (ii) Experimental as well as theoretical investigations of this molecule are scarce.

The instrument used in this work has fully been described elsewhere (1, 2). The kinetic energy distributions of C⁺ were recorded at different electron energies. The origin of the kinetic energy scale is calibrated by taking the maximum of the CO⁺ peak. Broad peaks with maxima at 0.1 aV, 0.5 eV and 3.0 eV are observed in the distribution of C⁺. The nearly thermal peak shifts to lower energies with decreasing the electron energy. Figure 1 shows two C⁺ energy distributions as determined close to threshold of both processes

\[
\text{CO} + e^- \rightarrow \text{CO}^* + e^- \rightarrow C^+(2\text{P}^0) + O^-(3\text{P}) \quad (I)
\]

and

\[
\text{CO} + e^- \rightarrow C^+(2\text{P}^0) + O^-(3\text{P}) \quad (II)
\]

Fig. 1 First differentiated retarding curve of C from CO at (1) 24 eV and (2) 22 eV.
In the energy distribution of the former process, the thermal peak coincides with the peak of CO⁺. Furthermore, both distributions exhibit a well pronounced fine structure which can only be ascribed to the predissociation of respectively (i) a super-excited neutral vibronic state of CO and (ii) a molecular ion state. The position in energy of the observed structure has been listed in table I. For comparison with spectroscopic data, only the total kinetic energy values have been listed, obtained by multiplying the measured kinetic energy by the ratio 28/16.

a) At 22 eV the C⁺ ion can only be produced by the ion pair process (I)

\[
\text{CO} + e^- \rightarrow \text{CO}^* (3d\sigma \text{Ryd}) + e^- \\
\rightarrow \text{C}^+(^3\text{P}^o) + \text{O}(^2\text{P})
\]

for which a threshold is calculated at 20.904 eV (3). The structure observed in the C⁺ ion energy distribution could be ascribed to the predissociation of the 3dσ Rydberg state's vibrational progression as observed by CODLING (4,5).

b) At 24 eV the C⁺ ion is mainly produced by the process

\[
\text{CO} + e^- \rightarrow \text{CO}^+(D^2 \Pi \text{pred.}) + 2e^- \\
\rightarrow \text{C}^+ (^3\text{p}^o) + \text{O}(^3\text{p})
\]

for which the threshold is calculated at 22.369 eV. As seen from table Ib, the observed structure is in good agreement with the kinetic energy deduced from the photoelectron spectroscopic data for the D^2 Π state of CO⁺ (4,5). The scarcity of data about the CO⁺ states does not allow an assignment of the predissociating state involved. With this purpose, measurements of the threshold energy of appearance of C from CO, as a function of the kinetic energy carried away by the fragment, are being performed

| TABLE I: Position of the submaxima (meV) observed in the kinetic energy distribution of C⁺ from CO. The quoted error is the standard deviation σ. |
|---|---|---|---|
| (a) Electron energy 21 eV - 23 eV | (b) Electron energy 24 - 30 eV | |
| This work | Absorpt.Spectr.* | This work | Photoelectr. Spectr.* |
| 0 ± 5 | (-34 ± 7) | 21 ± 7 | 16 ± 10 |
| 152 ± 24 | 156 ± 7 | 178 ± 26 | 183 ± 10 |
| 325 ± 35 | 336 ± 7 | 352 ± 17 | 350 ± 10 |
| 469 ± 23 | 512 ± 7 | 523 ± 31 | 516 ± 10 |
| 625 ± 40 | 649 ± 7 | 693 ± 21 | 686 ± 10 |
| 875 ± 24 | 851 ± 10 | 1052 ± 17 | 1003 ± 10 |
| 1052 ± 17 | | 1014 ± 10 | |

* calculated by using D(C⁺ - O) = 20.904 eV and D(C⁺ - O) = 22.369 eV

References


(2) R. LOCHT, J. SCHOPMAN, H. WANKENNE, J. MOMIGNY, Chem.Phys.in press

