LETTER TO THE EDITOR

Calculation of resonant vibrational excitation of CO by scattering of electrons

Mariusz Zubek and Czeslaw Szmytkowski
Institute of Physics, Technical University of Gdańsk, 80-952 Gdańsk, Poland

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Abstract. The cross sections for resonant vibrational excitation of the CO molecule by scattering of electrons have been calculated on the basis of the boomerang model of Herzenberg. The molecular parameters for the CO\(^{(2\Pi)}\) resonance are obtained from the fit to the experiment. For the average autoionization width \(\langle \Gamma \rangle\) the value of 0.6 eV has been found.

Studies of resonance states in molecules have revealed states having lifetimes comparable to typical vibrational periods (Schulz 1973, Boness and Schulz 1974). The lifetimes of these states are intermediate between the short-lived states (e.g. \(\text{H}_2\)(\(^{2}\Sigma_u^+\))\(\approx 10^{-15}\) s) and the long-lived states (e.g. \(\text{O}_2\)(\(^{2}\Pi_g\))\(\approx 10^{-10}\) s). Examples are the shape resonances \(\text{N}_2\)(\(^{2}\Pi_g\)) located around 2.3 eV, \(\text{CO}^-\)(\(^{2}\Pi\)) near 1.7 eV and \(\text{CO}_2\)(\(^{2}\Pi_u\)) near 3.8 eV. The characteristic feature of the energy dependence of the vibrational excitation by electron impact on \(\text{N}_2\), \(\text{CO}\) and \(\text{CO}_2\) is that the locations of the peaks in the cross section shift toward higher energies as the vibrational quantum number of the final state is increased.

A theoretical model—the boomerang model—for this type of state has been developed by Herzenberg (1968) and Birtwistle and Herzenberg (1971). It has been applied to \(\text{N}_2\) and relative vibrational cross sections have been obtained in excellent agreement with the experiment of Ehrhardt and Willmann (1967).

In this work we have tried to apply this model to electron scattering by CO in the energy range of the \(\text{CO}^-\)(\(^{2}\Pi\)) shape resonance (Schulz 1964, Ehrhardt et al 1968) formed by trapping the incident electron in a \(\pi\) orbital. The purpose of this letter is to confirm the application of the model to diatomic molecules as well as to determine parameters of the resonance state, particularly the autoionization width \(\Gamma\).

The calculations were made with the assumption that the resonant scattering has p-wave character (Ehrhardt et al 1968). The energy of the resonant state was written as \(E^- (R) = \frac{1}{2} i \Gamma (R)\) where a Morse curve was used for \(E^- (R)\) and \(\Gamma (R)\) was represented by the expression given by Blatt and Weisskopf (1952, p 390). The penetration factor for the angular momentum barrier in \(\Gamma\) was that corresponding to a p-wave barrier (Blatt and Weisskopf 1952, p 361). The dissociation energy of \(\text{CO}^-\) (8.25 eV) was deduced from the dissociation energy for the neutral molecule and the electron affinity of the O atom (the dissociation limit of the ion is probably \(\text{C}^{(3}\Pi) + \text{O}^- (^{2}\Pi)\)). The ‘radius’ of the \(\text{CO}^-\) ion was set to be 1.6 Å.
The main molecular parameters of the resonance state and the relative normalization of the numerically calculated and the experimental cross sections have been chosen to give the best fit between the calculations and the experimental results of Ehrhardt et al (1968). The parameters of the best fit are as follows:

\[ E^-(R_0) - E(R_0) = 1.52(\pm 0.02) \text{ eV} \]
\[ h\omega^- = 0.235(\pm 0.007) \text{ eV} \]
\[ R_0^- - R_0 = 0.092(\pm 0.002) \text{ Å} \]
\[ \Gamma(R_0) = 0.80(\pm 0.03) \text{ eV} \]

The errors are estimated from the variation between the fit and the parameters.

In figure 1 the calculated and experimental cross sections are compared; reasonable agreement is obtained. The differences in the curves for \( v = 1 \) may be explained by the direct scattering component which is clearly seen below 1 eV. The calculations are made for a pure resonant process.

The values of the potential parameters required for CO\(^-\) are close to those of N\(_2\) quoted by Birtwistle and Herzenberg (1971). It is not surprising that both ions are isoelectronic and the incoming electrons occupy a \( \pi \) orbital. The width \( \Gamma \) is a little higher than for N\(_2\) as a result of a broader potential barrier for \( l = 1 \).

\[ \text{Figure 1. Comparison of experimental cross sections (full curves, Ehrhardt et al 1968) and calculated cross sections (broken curves, this work).} \]
The contributions of the various partial waves to the angular distribution of this resonance in CO is discussed in several papers. Bardsley and Read (1968) suggested that both p\pi and d\pi waves might be important. A comparison made by Read (1968) of the theoretical expression for the angular distribution of resonance scattering with that obtained experimentally suggests the predominance of the partial p-wave over the d-wave. Vibrational cross sections calculated by the authors with the assumption that l = 2 have given a much worse fit with experiment than the calculations for l = 1, and the values of the parameters of that fit are less probable. Assuming the validity of the expression used to determine the penetration of the potential barrier by an electron, we can state that the calculations prove a greater contribution of the partial p-wave to the resonance scattering in the energy range investigated.

The mean value \langle \Gamma \rangle has also been calculated. It was found to increase slightly with increasing energy, and a value of 0.63 eV at an energy of 1.75 eV has been obtained.

Besides the vibrational cross sections we have also found a cross section for resonance elastic scattering of electrons. The peak positions in the elastic cross section are close to those observed by Boness and Hasted (1966) in transmission measurements (see table 1). Similar calculations made for elastic cross section in N\textsubscript{2} gave a good fit of the calculated peak positions to those measured by Ehrhardt and Willmann (1967) in elastic scattering.

By normalizing to the calculated vibrational cross sections we obtain a value of 12.7 Å\textsuperscript{2} for the peak of the elastic resonance cross section for CO.

The calculations have been carried out by an ICL computer in the ZIPO Computer Centre in Gdański. The authors thank Mr J Drewko for having prepared the program. This work is partly supported by the Institute of Physics of Warsaw University.

References

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Table 1. Energy positions (in eV) of the peaks in the cross sections for CO.

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<tr>
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<th>This work: elastic</th>
<th>Boness and Hasted: total</th>
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<tr>
<td></td>
<td>1.53 1.72 1.95 2.17 2.45</td>
<td>1.26 1.54 1.74 1.95 2.18 2.37</td>
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