[10]E. Merzbacher and H. W. Lewis, in Encyclopedia of Physics, edited by S. Flügge (Springer-Verlag, Berlin, Germany, 1958), Vol. 34, p. 166.

[11]M. Ya. Amusia, Zh. Tekh. Fiz. 36, 1049 (1966) [translation: Soviet Phys.—Tech. Phys. 11, 1053 (1967)].

ELECTRON-IMPACT EXCITATION OF CARBON MONOXIDE NEAR THRESHOLD IN THE 1.5- TO 3-eV INCIDENT ENERGY RANGE*

R. D. Rempt

Department of Physics, University of California, Los Angeles, California 90024
(Received 10 March 1969)

A low-energy excitation process in CO at approximately 2.3 eV is investigated near threshold by a trapped-electron method. Structure has been observed in this excitation for the first time. An upper limit to the electron affinity of CO is established at -1.8 ± 0.1 eV.

Excitation of carbon monoxide by electron impact in the region 1.5-3 eV incident electron energy has been studied by a trapped-electron method in which a rather small well depth of approximately 0.05 ± 0.03 V is maintained. A low-energy inelastic process peaking at about 2.3 eV is observed including structure as is shown in Fig. 1. This process has not been directly studied close to threshold before, and no structure has been observed near threshold by previous investigators. Schulz[1] has observed the phenomenon but not close to threshold. At least five "bumps" are clearly distinguishable with a spacing of approximately 0.2 eV. In the present work, it was found that increasing the well depth shifted the peak towards lower energy. At sufficiently large well depths where no vibrational structure could be observed in the $a^3\pi$ excitation (see below), this low-energy peak increased in magnitude and peaked at approximately 1.7 eV in agreement with the data of Schulz.

The type of device used in this experiment was a Tate-Smith ionization tube.[2] "Trapped-electron" spectra have been recorded in such a device.[3]

The estimation of the well depth is difficult and can hence lead to errors in the calibration of the electron energy. In the present experiment the well depth was kept sufficiently low to observe the vibrational fine structure of the $a^3\pi$ excitation. According to Herzberg[4] the $v = 0$ vibrational level for this state occurs at 6.01 eV. One method of calibrating the electron-energy axis is by assigning a value of 6.0 eV to this level. By extrapolating the electron beam current linearly to zero and establishing this intercept as zero energy, the $v = 0$ vibrational level of the $a^3\pi$ state occurs at 6.0 eV in agreement with the spectroscopic data of Herzberg[4] and the electron-impact

data of Brongersma and Oosterhoff.[5]

In Fig. 2 another method of energy calibration is shown. By increasing the voltage across the parallel plates, only negative ions can be collected at the collector plate.[6] The energy scale is calibrated by assuming the peak on the dissociative-attachment cross section occurs at 9.9 eV.[7] This mode of operation is much like that used by Rapp and Briglia.[8] In Fig. 2 the voltage across the plates is 6.2 V for the negative ions (open circles) which are taken at a sensitivity of 3.3 times the sensitivity of the trapped electrons. The voltage across the parallel plates for the trapped electrons is again zero. The peak at approximately 9.95 eV in the trapped-electron
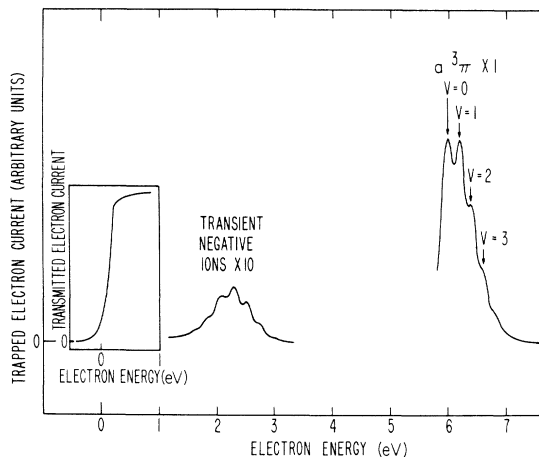

FIG. 1. Plot of trapped-electron current versus electron energy showing evidence of structure in transient negative-ion formation. Insert shows transmitted electron current. Calibration of electron-energy axis is obtained by linear extrapolation of transmitted electron current to zero, which places $v = 0$ vibrational level of $a^3\pi$ excitation at 6.0 eV.
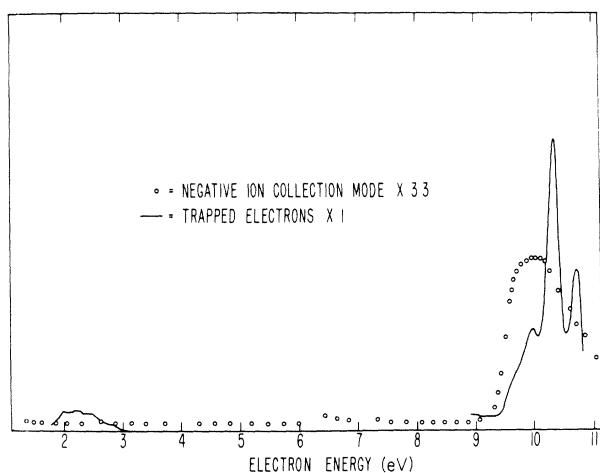
FIG. 2. Alternative method of calibrating electron-energy axis. The electron-energy axis is calibrated by placing the negative-ion peak at 9.9 eV. The "transient" negative ions again occur at $\simeq 2.3$ eV. Resolution and amplification of "transient" negative ions is not as great as in Fig. 1.

spectrum is from dissociative attachment, while the one occurring at ~10.4 eV is assigned to the excitation of the $b^3\Sigma^+$ state and the peak at ~10.8 eV is assigned to the excitation of the $B^1\Sigma^+$ state. These results are in agreement with those of Brongersma and Oosterhoff.[5] The low-energy excitation peaks again at approximately 2.3 eV, although in Fig. 2 the amplification and resolution are not as great as in Fig. 1.

Because of the geometry of the interaction region and the orientation of the electron beam with respect to the plates, "total collection" of trapped electrons cannot be ensured. Therefore the data shown cannot be interpreted as proportional to the total excitation cross section. The plot of negative ions in Fig. 2 is, however, proportional to the total cross section for dissociative attachment.

To interpret the series of peaks in the 2.3-eV region, all possible channels for energy loss of the incident electron must be considered. These possible channels are (1) direct electronic excitation, (2) direct vibrational excitation, (3) formation of a stable negative ion, and (4) formation of a "transient" negative ion. The lowest lying electronically excited state in CO lies at 6.01 eV.[4] This eliminates the possibility of channel 1.

The fact that the cross section for production of slow electrons of ~0.08-eV energy is essentially zero below ~1.5 eV would eliminate the possibility of channel 2. There is no a priori reason to assume that direct vibrational excitation should

occur by electron impact only in the region from 1.5 to 3 eV, since this would highly favor the excitation of the $v = 5$ through $v \approx 12$ vibrational states only.

In Fig. 1, no negative ions are observed in the 2.3-eV region. If this peak were due to stable negative ions it would have been 3 times as large when the apparatus was run in the "negative-ion collection mode," and it would have doubtless been observed by previous investigators studying negative ions. These facts rule out the possibility of channel 3.

Channel 4, the formation of a "transient" negative ion, remains as the only interpretation. In this experiment, an electron is collected only if it has lost all but 0.08 eV of its energy. Therefore one possible interpretation of the observed structure would be that a "bump" is observed whenever a vibrational level of the "transient" negative ion is coincident to within 0.08 eV of a vibrational level of the ground state of CO, assuming that the states of the "transient" negative ions are well defined. This is to say that an electron nears the molecule and temporarily attaches to the molecule in some vibrational state of the "transient" negative ion. A short time later the negative ion autodetaches and leaves the molecule in some vibrational state of the ground electronic state. If the ejected electron has ≈ 0.08 eV or less it is then collected. In his experiment, Schulz[9] studied electrons which had ~0.25 eV of energy or more after being ejected from the "transient" ion state. These electrons would leave the molecule in the lower lying vibrational states of the ground electronic state. Such electrons are not collected in the present experiment. It is difficult to compare the two experiments in that Schulz collected electrons which had been scattered through an angle of 72° and analyzed their energy loss, whereas in the present work only those electrons which retain approximately 0.05 ± 0.03 eV of their energy are collected over almost all scattering angles.

Since the lifetime of this "transient" ion is short, there may be a loss of definition in the various vibrational levels of this state. Therefore the state may not have to be within 0.08 eV of a vibrational level of the ground state of CO in order to cause a "bump." "Smearing" of "bumps" may therefore arise due to the fact that the levels of the "transient" ion state are not precisely defined. The resolution of the "bumps," however, is most likely limited by the 0.2-eV energy spread in the primary electron beam. The observed

structure is in striking agreement with that of Hall and Reinhardt[10] for the case of N_2 which is isoelectronic to CO.

The "bump" observed at the lowest energy occurs at the location of the ground state of the "transient" negative ion or higher. This would allow the assignment of an upper limit to the electron affinity of CO. In Fig. 1 there is a definite bump at 1.8 eV and possibly another at ~1.6 eV. This experiment assigns the value of -1.8 ± 0.1 eV as an upper limit for the electron affinity of CO. The possibility of another "bump" at 1.6 eV may reduce this value when greater sensitivity is achieved.

The author wishes to thank Professor Joseph Kaplan for continued support during the course of this research, and is deeply indebted to Professor Donald Villarejo for interesting and stimulating discussions concerning the interpretation of the data.

[1]G. J. Schulz, Phys. Rev. 116, 5, 1141 (1959).
[2]J. T. Tate and P. T. Smith, Phys. Rev. 39, 270 (1932).
[3]J. T. Dowell and T. E. Sharp, J. Chem. Phys. 47, 12, 5068 (1967).
[4]G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand Company, Inc., Princeton, N.J., 1950).
[5]H. H. Brongersma and L. J. Oosterhoff, Chem. Phys. Letters 1, 169 (1967).
[6]The mechanism by which the trapped electrons reach the collector plate is a diffusion mechanism due to collisions. An electron which lacks sufficient energy to escape in the axial direction collides with gas molecules until it finally reaches the collector plate or "center" plate of the parallel-plate assembly. It was observed that a small electric field of the order of ~1 V/cm made the trapped electrons vanish. This was attributed to the $\vec{E} \times \vec{B}$ drift velocity given to all charged particles within the region where the electric field exists. The value of the electric field at which the trapped-electron current vanishes together with the magnitude of the magnetic field and information concerning the width of the plates and their distance from the electron beam leads to an estimation of the rate of diffusion due to collisions across the magnetic field.
[7]The work of D. Rapp and D. D. Briglia [J. Chem. Phys. 43, 1480 (1965)] and the more recent work of P. J. Chantry [Phys. Rev. 172, 125 (1968)] both establish the position of the peak in dissociative attachment in CO at 9.9 eV.
[8]Rapp and Briglia, Ref. 7.
[9]G. J. Schulz, Phys. Rev. 135, A988 (1964).
[10]J. Hall and J. Reinhardt, Compt. Rend. B266, 744 (1968).

EXPANSION TECHNIQUE FOR INELASTIC SCATTERING*

Frank E. Harris
Department of Physics, University of Utah, Salt Lake City, Utah 84112

and

H. H. Michels
United Aircraft Research Laboratories, East Hartford, Connecticut 06108
(Received 3 January 1969)

A nonarbitrary method is presented for the calculation of inelastic-scattering wave functions by an expansion technique. The method can be applied for any incident energy, including values at resonances resulting from stable or metastable bound states. Calculations are presented for an exactly soluble two-channel model problem which illustrates the utility of the method.

A central objective in the development of expansion methods for treating nonrelativistic quantum-mechanical scattering is the identification of optimum criteria for defining the expansion coefficients. The well-known variational methods of Kohn[1] and Hulthén[2] are arbitrary in the sense that they are two of an infinite set of prescriptions leading to phase shifts whose errors are of second order. Moreover, the variational criterion alone is not sufficient to guarantee in any reasonable sense an optimum wave function, as is evidenced by the convergence problems[3] exhibited by the Kohn method. The difficulties are, at least in part, due to the approximation of a continuous-spectrum Hamiltonian by a finite-dimensional projection thereof whose discrete spectrum does not necessarily contain an a priori-selected scattering energy. This consideration led one of the present authors to propose a method for selecting scattering en-