PHYSICAL REVIEW
LETTERS

VOLUME 26 | 19 APRIL 1971 | NUMBER 16

New Resonances in the Total Cross Section of Electrons on CO and O_2 †

L. Sanche and G. J. Schulz
Mason Laboratory, Yale University, New Haven, Connecticut 06520
(Received 2 February 1971)

A transmission experiment is used to observe the structure in the total electron-impact cross section in CO and O_2. The structure in the cross sections is enhanced by measuring directly the derivative of the transmitted current. An isolated resonance in CO is observed at an electron energy of 10.04 ± 0.03 eV. In O_2, structure is observed which correlates well with the absorption spectra in the energy range 8-10 eV. In addition, two very sharp resonances (30-meV width) are observed at 8.02 ± 0.03 and at 8.25 ± 0.03 eV.

Resonances in the total cross section for electron impact on diatomic molecules have been the subject of extensive experimental and theoretical investigations in recent years. These resonances can be classified into two major categories,[1] namely, (i) "single-particle" or "shape" resonances which consist of the target molecule, usually in its ground electronic state, plus an electron trapped in the neighborhood of the molecule by the centrifugal barrier and polarization and exchange potentials, and (ii) "core-excited" or Feshbach-type resonances which consist of an electron temporarily bound to an excited state of the molecule. Whereas single-particle resonances generally lie 0-3 eV above the ground state, core-excited resonances lie at higher energies, near the excited state from which they derive. This Letter reports observations of new resonances in the energy range 8-10 eV in both O_2 and CO.

Experiment.—The existence of resonances can be established by observing structure in either the elastic or inelastic cross sections by electron impact, and by studying vibrational excitation or dissociative attachment. We examined the structure in the total electron-impact cross section using a transmission experiment. Such an experiment can be used to enhance the structure in the cross section as described by Kuyatt, Simpson, and Mielczarek[2] and by Schulz.[3] A further refinement is introduced in the present experiment by observing directly the derivative of the transmitted current.

Figure 1 shows a diagram of the apparatus. Electrons emitted from a thoria-coated iridium filament F are aligned by an axial magnetic field B of 130 G and traverse a trochoidal monochromator[4] to produce a monoenergetic electron beam of about 3×10^{-9} A with an energy spread between 25 and 40 meV. The electrons leaving the mono-

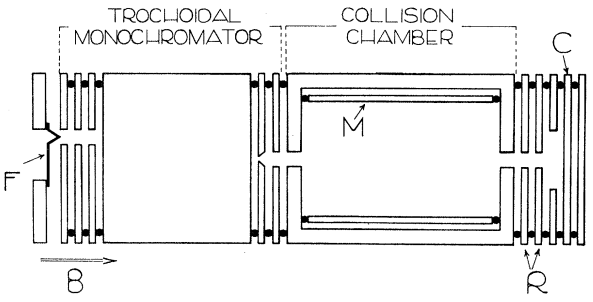

FIG. 1. Schematic diagram of transmission tube. Electrons are emitted from the filament F and aligned by a magnetic field B and pass through the trochoidal monochromator and the collision chamber. A small modulating signal (5-50 meV, 71 Hz) is applied to M and the transmitted current is detected synchronously at the collector C. The retarding electrodes R provide a potential barrier for scattered electrons.

chromator are accelerated into a collision chamber maintained at a pressure of about 0.03 Torr. Those electrons which reach the exit of the collision chamber are decelerated to nearly zero energy by the two retarding electrodes R. This deceleration prevents scattered electrons from reaching the electron collector C because the scattered electrons have their velocity vector reoriented and thus do not possess sufficient axial momentum to overcome the potential barrier.

Unlike the conventional transmission experiment, which measures directly the transmitted current, the technique used for this work measures the *derivative* of the transmitted current. A sine wave of variable amplitude (5-50 meV peak-to-peak) is applied between the collision chamber and the insulated cylinder M surrounding the inside of the collision chamber. The resulting modulation in the transmitted current measured on electrode C is amplified by an operational amplifier and measured in phase with the modulating signal by means of a phase-sensitive detector. During each sweep the modulating signal is kept constant, and thus the output signal from the phase-sensitive detector is directly proportional to the derivative of the transmitted current taken with respect to the electron energy. A more complete description of this technique will be given in a future publication.

Structure in the derivative of the transmitted current may be due to the following causes: (i) resonances in either the elastic or inelastic cross section; (ii) rapid changes in the inelastic cross section not related to resonances, e.g., sharp onsets, or variations in the Franck-Condon factors in molecular transitions. Resonances and sharp onsets can be recognized by the shape of the structure they produce in the derivative of the transmitted current. However, difficulties in the interpretation of the data may arise when the above-mentioned structures overlap. In this case, we make an attempt to correlate the data with known inelastic thresholds and other observations in order to arrive at a proper interpretation. Sharp resonances are usually not afflicted by these problems and are easy to identify. We have checked the procedure outlined above in the case of helium, where most resonances are fairly well known. We can reproduce all the features found by Kuyatt, Simpson, and Mielczarek[2] with a signal-to-noise ratio about an order of magnitude better. There are no significant discrepancies in the energy scale. In the case of CO the interpretation of our results is essentially unambiguous, whereas O_2 represents a more difficult problem of interpretation.

Resonance in CO. – Figure 2 shows a plot of the derivative of the transmitted electron current versus energy. The structure at about 6 eV is interpreted as the excitation of vibrational levels of the $a\,^3\Pi$ state of CO. Trapped-electron experiments also show this structure.[5] The known positions of these vibrational levels[6] are indicated on the upper portion of the figure. No further structure is evident until we come to the large excursion around 10 eV. We can identify this structure as a resonance whose shape is broader than the spread in the electron beam. Without a complete phase-shift analysis, we can only estimate the natural width to be of the order of 0.04 ± 0.02 eV. The energy position of this resonance has been established in three different ways: (1) by comparison with the 19.30-eV resonance[3] in He using a CO + He gas mixture, (2) by comparison with the 11.09-eV argon resonance[2] using a Co + Ar gas mixture, and (3) by measuring the energy difference between the onset of the $a\,^3\Pi$ state and the resonance. All three calibrations agree within 30 meV and lead to the value 10.04 ± 0.03 eV for the energy at which the derivative curve has a minimum. The maximum of the transmitted current would occur at the position at which the derivative curve goes through the first zero, i.e., at 10.00 ± 0.03 eV. The *center* of the resonance lies between the maximum and the minimum of the transmitted current, i.e.,

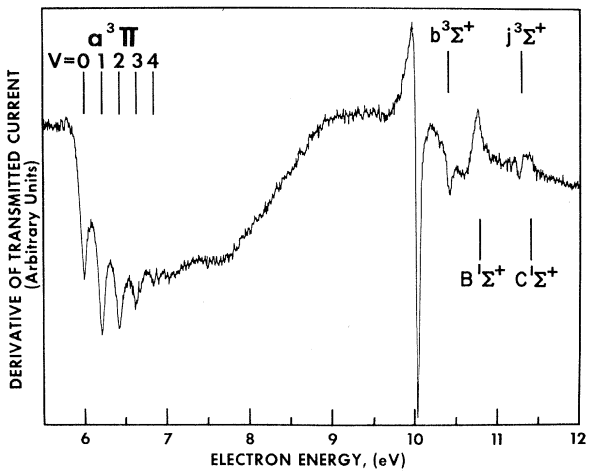

FIG. 2. Derivative of the transmitted current versus electron energy in CO. The structure in the region 6-7 eV is due to inelastic processes involving the $a\,^3\Pi$ state. The sharp structure around 10.04 eV is a new resonance. The locations of some of the electronic states of CO are indicated.

close to the minimum in the derivative at 10.04 eV.

The dip which follows the resonance occurs at 10.40 ± 0.03 eV, in agreement with the spectroscopic location[6] of the $b\,^3\Sigma^+$ state (10.39 eV). Assignment of emission lines from that state indicate that only the ground and first vibrational levels of the $b\,^3\Sigma^+$ state are excited. It therefore seems likely that the $b\,^3\Sigma^+$ state is the parent of the 10-eV resonance, since that resonance also has little vibrational structure.

Furthermore, the nature of the structure at 10.40 eV indicates the presence of a sharp onset, possibly with a peak, in the excitation cross section of the $b\,^3\Sigma^+$ state. In N_2, our data show a markedly similar behavior for the excitation of the $E\,^3\Sigma_g^+$ state at 11.87 eV, with a resonance[7] lying near 11.4 eV. The sharp threshold behavior of the cross section for the electron excitation of the $E\,^3\Sigma_g^+$ in N_2 has been previously observed by Heideman, Kuyatt, and Chamberlain[7] and confirmed by other types of experiments.[5,8,9] The trapped-electron data of Brongersma and Oosterhoff[5] also show a similarity in the threshold behavior of the $^3\Sigma^+$ cross sections in CO and N_2. Thus it appears that in both CO and N_2 a resonance lies about 400 meV below the respective $^3\Sigma^+$ states and that the inelastic cross sections for the excitation of the $^3\Sigma^+$ states exhibits a resonant-type behavior near threshold.

It is now known that the existence of a resonance below an inelastic threshold can cause sharp structure in the inelastic cross section just above threshold.[10] This effect is caused by a new channel of decay opening up at the threshold of the inelastic process, leading to a sudden increase in decay width for the resonance. Such an effect is expected only when the excited state is the "parent" of the compound state. We can speculate that the behavior of the excitation cross section for the $^3\Sigma^+$ states in both CO and N_2 is caused by the existence of the resonances lying below these states.

The fact that the 10-eV resonance does not seem to have significant vibrational structure could indicate that the shape of the CO^- potential-energy curve to which the resonance belongs has a small well in the Franck-Condon region and a potential "hump" at larger internuclear separations. The "hump" could arise from an avoided crossing between two states of the same symmetry, and the potential could be deep enough to support a single vibrational state. Such a hypothesis is consistent with the data of Stamatovic and Schulz[11] who found that the onset of C^- production from CO is delayed by 0.36 eV, a value which is indicative of the height of the "hump." Furthermore, the presence of the resonance at 10 eV would explain the structure they observe at that energy in the cross section for O^- formation from CO. The remaining structure in CO seems to occur in the inelastic cross section, as may be seen from the agreement with the energy position of the absorption lines taken from the recent work of Tilford and Vanderslice.[12]

Resonances in O_2.—Figure 3 shows a direct plot of the derivative of the electron transmission spectrum of O_2 between 8 and 10 eV. The observed structure can be compared with the peaks observed in optical absorption, and fairly good correspondence can be found. Exceptions are the two very sharp structures at 8.02 and 8.25 ± 0.03 eV, respectively. The widths of the rising portion of these structures are limited by the spread in the electron beam (about 30 meV). The existence of these compound states would imply that at least one parent electronic state of O_2 exists around 8.3-9.0 eV. No spectroscopic or theoreti-

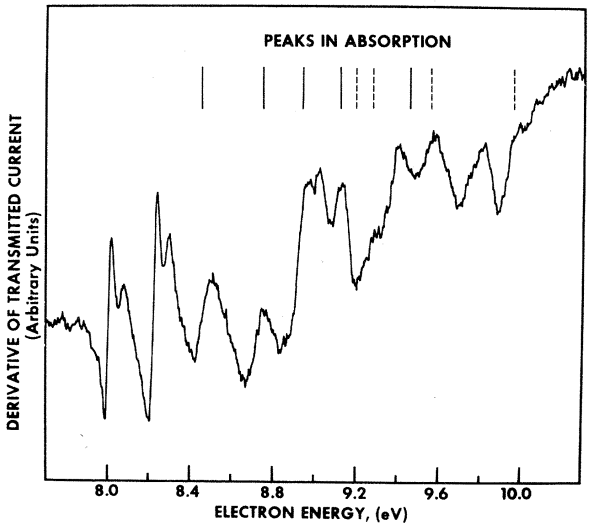

FIG. 3. Derivative of the transmitted current versus electron energy in O_2. The two sharp structures near 8.02 and 8.25 eV are interpreted as sharp resonances. Most of the remainder of the structure probably results from "undulations" in the Franck-Condon factors. The peaks in photon absorption observed by Bixon, Raz, and Jortner (Ref. 13) are indicated by the vertical solid lines, and the prominent absorption peaks observed by Tanaka (Ref. 14) are shown by the dashed lines. For calibrating the energy scale, a small amount of either He or Ne is admixed to O_2 and the 19.30-eV resonance in He and the 11.09-eV resonance in Ar are used as calibration points. The energy scale is accurate to ± 0.03 eV.

cal evidence exists for bound excited states in this energy range.[15] It is therefore difficult to interpret the two sharp structures at 8.02 and 8.25 eV in the usual fashion, and no clear-cut answer can be provided. The possibility exists that the two resonances result from an avoided crossing of two O_2^- potential-energy curves, which may lead to a well of sufficient depth to support two vibrational modes.

Condon[16] has shown that Franck-Condon factors associated with repulsive-type curves can exhibit undulations which he called "diffraction bands in the continuous spectrum." These have been recently confirmed theoretically[13,17] and observed experimentally.[13,17,18] In fact, electron beam experiments also could be interpreted in this fashion.[19,20] The absorption peaks resulting from "undulations" and measured by Bixon, Raz, and Jortner[13] are indicated in Fig. 3 by the vertical solid lines and the strongest absorption peaks of Tanaka[14] by the vertical dashed lines. Fair agreement exists between the absorption peaks and the structure found in the present experiment. The two sharp structures at 8.02 and 8.25 eV seem to be exceptions, and their sharpness would indicate that they do not result from "diffraction" effects.

The authors are indebted to P. D. Burrow and A. Herzenberg for advice and helpful comments. Also, thanks are due to J. H. Kearney for technical assistance.

†This work supported by DASA through the U. S. Army Research Office (Durham).

[1]H. S. Taylor, G. V. Nazaroff, and A. Golebiewski, J. Chem. Phys. 45, 2872 (1966).

[2]C. E. Kuyatt, J. A. Simpson, and S. R. Mielczarek, Phys. Rev. 138, A385 (1965).

[3]G. J. Schulz, Phys. Rev. 136, A650 (1964).

[4]A. Stamatovic and G. J. Schulz, Rev. Sci. Instrum. 39, 1752 (1968), and 41, 423 (1970).

[5]H. H. Brongersma, A. J. H. Boerboom, and J. Kistemaker, Physica (Utrecht) 44, 449 (1969). See also H. H. Brongersma and L. J. Oosterhoff, Chem. Phys. Lett. 1, 169 (1967).

[6]P. H. Krupenie, *The Band Spectrum of Carbon Monoxide*, U. S. National Bureau of Standards, National Standards Reference Data Series—5 (U.S.G.P.O., Washington, D. C., 1966).

[7]H. G. M. Heideman, C. E. Kuyatt, and G. E. Chamberlain, J. Chem. Phys. 44, 355 (1966).

[8]R. I. Hall, J. Mazeau, J. Reinhardt, and C. Schermann, J. Phys. B: Proc. Phys. Soc., London 3, 991 (1970). These authors observed the threshold excitation spectrum of N_2 by electron impact using the trapped-electron method.

[9]For evidence on the existence of resonant structure in the production of metastable N_2, see W. L. Borst and E. C. Zipf, Phys. Rev. A 3, 979 (1971); also, R. Clampitt and A. S. Newton, J. Chem. Phys. 50, 1967 (1969).

[10]H. Ehrhardt, L. Langhans, F. Linder, Z. Phys. 214, 179 (1968).

[11]A. Stamatovic and G. J. Schulz, J. Chem. Phys. 53, 2663 (1970).

[12]S. G. Tilford and J. T. Vanderslice, J. Mol. Spectrosc. 26, 419 (1968).

[13]M. Bixon, B. Raz, and J. Jortner, Mol. Phys. 17, 593 (1969).

[14]Y. Tanaka, J. Chem. Phys. 20, 1728 (1952).

[15]H. F. Schaefer III and F. E. Harris, J. Chem. Phys. 48, 4946 (1968).

[16]E. U. Condon, Phys. Rev. 32, 858 (1928).

[17]A. Dalgarno, G. Herzberg, and T. L. Stephens, Astrophys. J. 162, L49 (1970).

[18]R. Goldstein and F. N. Mastrup, J. Opt. Soc. Amer. 56, 765 (1966).

[19]J. Geiger and B. Schroder, J. Chem. Phys. 49, 740 (1968).

[20]G. J. Schulz and J. T. Dowell, Phys. Rev. 128, 174 (1962).

Complete Hyperfine Structure of a Molecular Iodine Line*

T. W. Hänsch,† M. D. Levenson,‡ and A. L. Schawlow§
Department of Physics, Stanford University, Stanford, California 94305
(Received 1 February 1971)

The complete hyperfine structure of the $P(117)$ line of the 21-1 band of the $B \leftarrow X$ transition of $^{127}I_2$ is observed at 568.2 nm. A resolution in excess of 10^8 is obtained by a sensitive technique of saturation spectroscopy using a krypton-ion laser. The spectrum can be fitted by a model which includes both a nuclear electric quadrupole and a magnetic hyperfine interaction.

The hyperfine structure in the visible absorption spectrum of molecular vapors is usually masked by Doppler broadening.[1] The techniques of laser-saturated absorption[2-4] offer a way, however, to overcome this difficulty. By studying inverted Lamb dips in a 632.8-nm He-Ne laser with an iodine-vapor absorption cell placed inside the cavity, Hanes and Dahlstrom[5] were