PHYSICAL REVIEW A VOLUME 8, NUMBER 6 DECEMBER 1973

Excitation of High Vibrational States of N_2 and CO via Shape Resonances*

M. J. W. Boness† and G. J. Schulz
Department of Engineering and Applied Science, Mason Laboratory, Yale University, New Haven, Connecticut 06520

(Received 14 August 1973)

The vibrational cross section to $v = 8$, 9, and 10 by electron impact on N_2 and CO has been measured in the energy range 2–4 eV. In this energy range vibrational excitation proceeds predominantly via a compound state, and decay into high vibrational states can occur. At the first peak the ratio of cross sections for $v = 8 : 9 : 10$ is $1 : 0.31 : 0.11$ in N_2, and $1 : 0.51 : 0.25$ in CO. These ratios are largely determined by the quantum-mechanical penetration through the centrifugal barrier.

I. INTRODUCTION

Vibrational excitation by electron impact on N_2 and CO is now well understood. Being isoelectronic, N_2 and CO exhibit similar behavior with respect to electron impact at low energies (0–5 eV). The bulk of the vibrational cross section at low energies for either N_2 or CO proceeds via a shape resonance. In N_2 this shape resonance has a configuration $^2\Pi_g$ and is centered around 2.3 eV whereas in CO the resonance has the configuration $^2\Pi$ and is centered around 1.7 eV. The energy dependence of the cross section for the first seven or eight states exhibits an oscillatory behavior which can be understood in terms of the "boomerang" model of Birtwistle and Herzenberg.[1] The above topics have been the subject of a recent review paper[2] and the reader is referred to this review for a listing of the original references.

In this paper we report measurements of the cross sections for higher vibrational states of N_2 and CO ($v = 8, 9, 10$), which we can now perform because of the improved detection sensitivity of our apparatus. The need for these cross sections arises from a desire to analyze electron-distribution functions in CO discharges which lead to laser action.[3] For such an analysis, one needs to know all vibrational cross sections in the energy range up to about 5 eV. In discharges employing CO_2 as the laser medium, N_2 is used as a pumping source and CO is present as a result of the dissociation of CO_2. However, in such discharges the high vibrational states discussed in this paper seem to play only a subsidiary role.[4]

II. EXPERIMENT

The apparatus used for this experiment consists of a double electrostatic analyzer, which is similar to the systems described previously.[5] The details of the present apparatus will be described elsewhere. Briefly, the instrument consists of a hemispherical monochromator which produces an electron beam with an intensity of 5×10^{-9} A and a half-width of 30 mV. This beam is focused using electron lenses onto a molecular beam which crosses the path of the electron beam. Electrons scattered into a given solid angle are focused by means of lenses onto the entrance of a hemispherical electron-energy analyzer, which is used to analyze the energy of the scattered electrons. After passage through this analyzer electrons impinge on the channeltron multiplier, where they are multiplied and the pulses are counted. Long-term averaging of the pulses is accomplished by sweeping the energy of the incident electrons repetitively and storing the accumulated counts in the memory of a small computer. The electron-energy analyzer is set to transmit those electrons which have lost energy to a specified vibrational level of the target molecule. We can then study the dependence upon incident electron energy for a given energy-loss process.

III. RESULTS

Figure 1 shows the energy dependence of the vibrational cross sections for excitation of the $v = 7$–10 vibrational levels of the N_2 molecule, in the range of the $^2\Pi_g$ compound state. The cross sections to $v = 7$ and $v = 8$ have been previously measured, but Fig. 1 presents a considerable improvement in signal-to-noise ratio. Thus much more detail can be seen in the cross sections for $v = 7$ and $v = 8$ than was possible previously. The cross sections for $v = 9$ and $v = 10$ have not been observed previously. Figure 2 presents similar results for CO.

In both N_2 and CO the positions of the peaks shift in energy. The first and subsequent peaks shift to higher energies for higher final vibrational states. This shift is completely consistent with earlier experimental observations[6-8] and with theory.[1]

IV. MAGNITUDE OF CROSS SECTIONS

In the present experiment we did not determine the absolute magnitude of the vibrational cross sections. Rather, we normalized our measurements to results obtained previously by various authors. Figures 3 and 4 show for N_2 and CO, respectively, a plot of the magnitude of the cross sections at the *first peak* of the vibrational excitation function, plotted against the quantum number of the vibrational state.

For N_2 (Fig. 3) we normalize all experimental data to the value given for $v = 1$ by Schulz,[6] who presented the vibrational cross section integrated over all angles. The absolute value of this cross section is based on the values obtained by Haas[9] and agrees well with the cross section obtained by Engelhardt, Phelps, and Risk[10] from swarm experiments.

The plot of Fig. 3 includes, in addition to the data of Schulz, the data of Ehrhardt and Willmann[7] for a scattering angle of 20° and data obtained in the present experiment at 23° and 90°. A plot like Fig. 3 in which observations at various angles are normalized to a common value makes a sensible comparison between experiments only if the angular distribution of electrons is the same for all vibrational levels. This should be the case, since the angular distribution is a property of the electronic state and should not depend on the quantum number of the final vibrational state. Nevertheless, if one examines with care the angular distributions obtained by Ehrhardt and Willmann,[7] one can detect differences in the angular distributions.[11] We are not certain whether these deviations are of instrumental origin, but we have not taken them into consideration. We have plotted the cross sections in Fig. 3 with the assumption that angular distributions do not vary for different vibrational states.

In Fig. 4 we show a plot of the cross section at the first peak versus vibrational state for the case of CO. We normalize all experimental points to the absolute value of the integrated vibrational cross section for $v = 1$. The actual value we choose is that of Ehrhardt *et al.*[8] In contrast to the case of N_2, the angular distributions obtained by Ehrhardt *et al.*[8] do not depend on the vibrational level which is produced. Nevertheless, there is a significant discrepancy between the data of Ehrhardt *et al.* and the present data on one side and

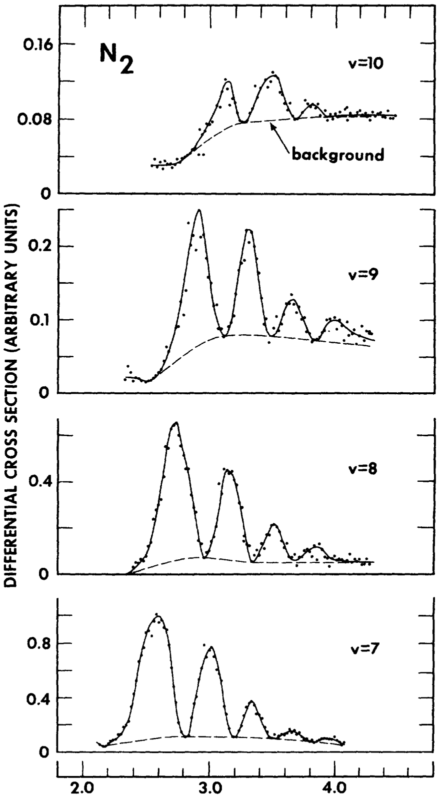

FIG. 1. Energy dependence of vibrational cross sections for $v = 7$–10 in N_2 taken at a scattering angle of 90°. The four cross-section curves are drawn on a compatible scale. The dashed curve indicates the background current, which is instrumental.

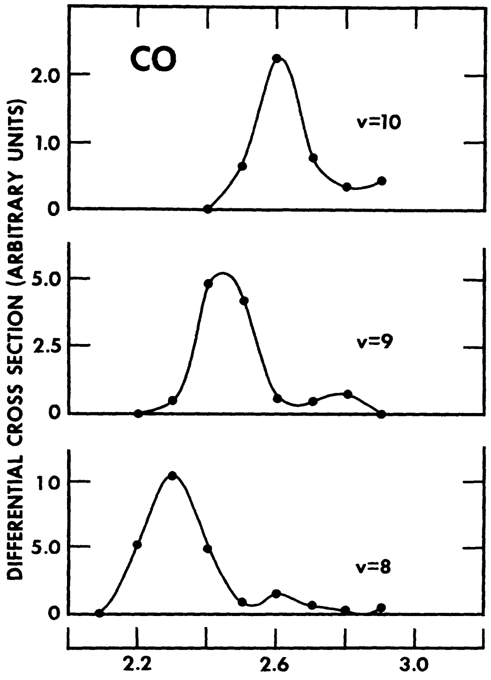

FIG. 2. Energy dependence of vibrational cross sections for $v = 8$–10 in CO, taken at a scattering angle of 90°.

the data of Schulz on the other. The deviation increases as final vibrational state increases. Since the excitation of higher vibrational state implies the production of a lower-energy electron, the discrepancy could be attributed to the different discrimination properties of various instruments, with respect to energy. The early experiment of Schulz did not employ electron lenses and, as a result, the electrostatic analyzer showed a preference for accepting lower-energy electrons. Conversely, our present apparatus uses electron lenses and we know from other experiments that it discriminates in favor of higher-energy electrons. Since our present data in CO agree with those of Ehrhardt and Willmann, we assume that their instrument must have had properties similar to our present one.

V. BARRIER PENETRATION

The relative cross sections for exciting different final vibrational states via a given resonance state are determined by the matrix elements and by the probability of penetration through the centrifugal barrier. For *high final vibrational states*, the matrix elements probaly do not vary significantly in order of magnitude, and we assume that the barrier penetration is the dominant factor. The probability of penetration through a centrifugal barrier can be approximated by the following expression[12]:

$$T \cong 4(\epsilon/E)^{1/2}\alpha_l \,. \tag{1}$$

Here ϵ is the energy of the departing electron and E is the sum of the incident electron energy and the potential energy inside the atom. Equation (1) is valid only if $\epsilon \ll E$, which is certainly satisfied when high vibrational states are excited. The factor α_l depends on the partial wave l, which is dominant. Blatt and Weisskopf[12] list the expressions for the factor α_l for different partial waves l. The partial wave[2,8] involved in the case of N_2 is a d wave ($l=2$) and in the case of CO it is predominantly a p wave ($l=1$). With the restriction that $R(2m\epsilon/\hbar^2)^{1/2} < 1$, we can write[12]

$$\begin{aligned} &\alpha_1 \sim \epsilon \quad \text{for } l=1, \\ &\alpha_2 \sim \epsilon^2 \quad \text{for } l=2. \end{aligned} \tag{2}$$

Above, R is a cutoff radius. The transmission coefficients then satisfy the proportionality

$$T_1 \sim \epsilon^{3/2}/E^{1/2} \quad \text{for CO,} \tag{3}$$

$$T_2 \sim \epsilon^{5/2}/E^{1/2} \quad \text{for } N_2. \tag{4}$$

The variation of $E^{1/2}$ is small over the energy range of interest,[13] and the dominant variation for the transmission coefficients comes from the variation of the energy of the departing electron,

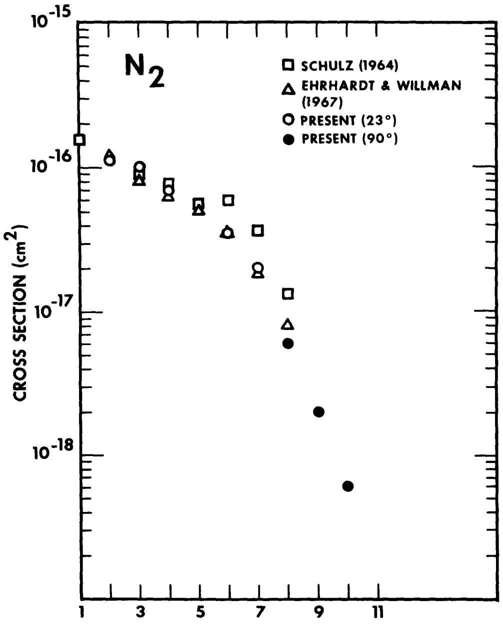

FIG. 3. Magnitude of the first peak in the vibrational excitation of N_2 vs quantum number of the vibrational state, $v=1$–10. Shown are the data of Schulz (Ref. 6) and of Ehrhardt and Willmann (Ref. 7), and the present data, all normalized to the cross section for $v=1$, given by Schulz (Ref. 6).

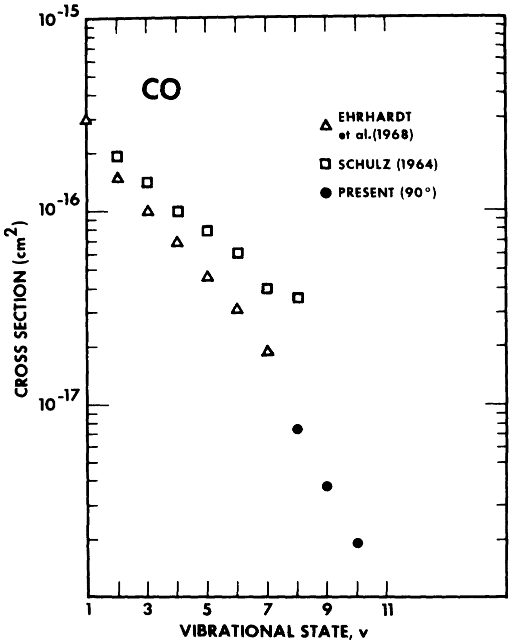

FIG. 4. Magnitude of the first peak in the vibrational excitation of CO vs quantum number of the vibrational state, $v=1$–10. Normalization is performed at $v=1$ to the cross section given by Ehrhardt *et al.* (Ref. 8).

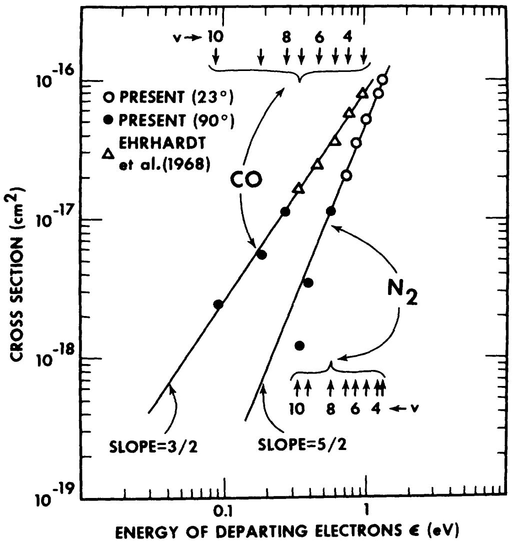

FIG. 5. Magnitude of the first peak in the vibrational cross section in N_2 vs the energy of the electron after the collision, ϵ. Under the assumptions discussed in the text, such a plot should give a straight line for high vibrational states, with a slope of $\frac{3}{2}$ for CO and $\frac{5}{2}$ for N_2. The straight lines have the slopes indicated in the figure.

ϵ. We plot in Fig. 5 the magnitude of the vibrational cross section at the first peak as a function of ϵ, on a log-log scale. The energy of the departing electron, ϵ, is the difference between the energy of the first peak in the vibrational excitation and the energy of the vibrational level, computed from the spectroscopic constants given by Herzberg.[14]

Straight lines with a slope of $\frac{3}{2}$ (applicable to CO) and a slope of $\frac{5}{2}$ (applicable to N_2) are drawn through the experimental points. To the extent that the experimental points lie on a line with the proper slope, we find agreement between the theory presented above and the experiment. That the lowest point of the N_2 curve does not lie on the straight line with slope $\frac{5}{2}$ is not too significant: The cross section for $v = 10$ is small and it is difficult to determine the exact energy for the first peak of the cross section in Fig. 5. This energy must be known in order to determine ϵ.

VI. CONCLUSIONS

Measurements have been made of the cross sections to high vibrational states in N_2 and CO by electron impact. The bulk of the vibrational excitation in the energy range 1–4 eV proceeds via compound states. The ratio of cross sections to *high vibrational states* seems to be dominated by the quantum-mechanical penetration through the centrifugal barrier which the departing electron must overcome in order to leave the compound state. The extrapolation of plots similar to Fig. 5 can provide the magnitudes of the cross sections for higher-lying vibrational levels which are not accessible to measurement owing to a lack of sufficient detection sensitivity. Such an extrapolation can be used provided that the levels are energetically accessible via a resonance mechanism, and provided that the approximations used in the derivation of the formulas are satisfied. Alternatively, one could use plots such as shown in Fig. 5 to determine the partial wave in which resonance scattering occurs.

ACKNOWLEDGMENTS

We are grateful to A. Herzenberg, P. D. Burrow, S. F. Wong, and J. Comer for many helpful comments and suggestions and to Charles Minter for developing the computer program used for data accumulation.

---

[*] Work supported by the Office of Naval Research.

[†] Present address: Avco Everett Research Laboratory, Everett, Mass. 02149.

[1] D. T. Birtwistle and A. Herzenberg, J. Phys. B 4, 53 (1971).

[2] G. J. Schulz, Rev. Mod. Phys. 45, 423 (1973).

[3] For the most recent discussion, see S. D. Rockwood, J. E. Brau, W. A. Proctor, and G. H. Canavan, IEEE J. Quantum Electronics QE-9, 120 (1973).

[4] W. L. Nighan, Phys. Rev. A 2, 1989 (1970).

[5] See, e.g., Z. Pavlovic, M. J. W. Boness, A. Herzenberg, and G. J. Schulz, Phys. Rev. A 6, 676 (1972).

[6] G. J. Schulz, Phys. Rev. 135, A988 (1964).

[7] H. Ehrhardt and K. Willmann, Z. Phys. 204, 462 (1967).

[8] H. Ehrhardt, L. Langhans, F. Linder, and H. S. Taylor, Phys. Rev. 173, 222 (1968).

[9] R. Haas, Z. Phys. 148, 177 (1957).

[10] A. G. Engelhardt, A. V. Phelps, and C. G. Risk, Phys. Rev. 135, A1566 (1964).

[11] We are indebted to J. Comer for pointing out to us that the angular distributions for N_2 (Ref. 7) depend on the vibrational level which becomes excited. A large deviation occurs between the angular distribution for $v = 1$ on one side and all other levels on the other side. One could expect some interference between direct and resonance scattering for $v = 1$, but then one could not explain the good fit obtained by fitting a pure resonance expression (Ref. 7) for $l = 2$ to the $v = 1$ angular distribution. Thus it appears that this phenomenon is not completely understood at the present time.

[12] J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics* (Wiley, New York, 1952), p. 361.

[13] J. N. Bardsley, F. Mandl, and A. R. Wood, Chem. Phys. Lett. 1, 359 (1967).

[14] G. Herzberg, *The Spectra of Diatomic Molecules* (Van Nostrand, Princeton, N.J., 1967).