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Rotational and Vibrational Excitation of Molecules by Low-Energy Electrons*

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Techniques for the determination of rotational and vibrational excitation cross sections of molecules by low-energy electrons are reviewed. The results of experiment are then compared with theory. High-energy resolution electron beam techniques are most useful for the measurement of the details of resonance-type, vibrational excitation cross sections. Cross section determinations from analyses of electron transport coefficients are most successful at energies near the threshold of vibrational excitation and for rotational excitation. High-frequency energy relaxation studies provide data on rotational excitation. A comparison of presently available experimental and theoretical results shows that some of the excitation processes, e.g., rotational excitation of N_2 and CO and vibrational excitation of CO near threshold, are accurately described by the longest-range forces and Born approximation. In other cases, e.g., vibrational excitation of N_2 and CO near 2 eV, the excitation is best described in terms of an electron resonance with the molecular potential.

I. INTRODUCTION

This paper compares the results of recent experimental and theoretical studies of the rotational and vibrational excitation of simple molecules by low-energy electrons. The importance of rotational and vibrational excitation in the description of the motion of low-energy electrons through molecular gases has been recognized for many years.[1,2] However, the small amount of energy lost by the electrons, the relatively poor fractional energy resolution available at low electron energies and the absence of, or low intensity of, radiation from the excited states have made experimental studies of rotational and vibrational excitation very difficult. Considerable progress has been made since this subject was reviewed by Craggs and Massey[2] in 1959. We first discuss briefly some of the experimental techniques by which the cross sections for rotational and vibrational excitation are determined. We then discuss the results obtained to date for homonuclear and heteronuclear molecules. The less familiar analysis of data obtained by the swarm technique is reviewed in the Appendix.

II. EXPERIMENTAL TECHNIQUES

The first of the techniques for the determination of electron excitation cross sections which we mention is the electron beam technique.[3] In this technique one determines the inelastic cross section from measurements of the rate of production of electrons which have lost the excitation energy in collisions with the gas molecules. The collisions may occur in a chamber filled with the gas under study at densities of approximately 10^{12} to 10^{13} molecules/cc or a beam of neutral molecules may be injected into the collision chamber so as to intersect the electron beam. One analyzes the energy distribution of the electrons observed at a given angle or over a range of angles. The ratio of the current of electrons which have lost energy corresponding to the excitation of a vibrational state to the current of electrons which have not lost energy is used along with measurements of total scattering cross sections from other experiments to calculate the vibrational excitation cross sections. The minimum electron energy to which this technique has been applied is about 0.2 eV. The energy spread of the incident electrons in these experiments is approximately 0.1 eV although lower energy spreads can be obtained with the more chemically inert gases.

A modification of the electron beam technique which has been used in a few studies of vibrational excitation is the multiple scattering or diffusion technique of Maier-Leibnitz.[4] Electrons of the desired energy are injected into a region free of electric fields. In these experiments the gas density is high enough so that the electrons which cross the tube undergo 20 to 100 elastic scattering events. A small fraction of these collisions are inelastic collisions and result in the loss of electron energy. The inelastically and elastically scattered components of the current are separated by the use of retarding potentials at the electron collector. The attenuation of the elastically scattered component is then used to calculate the inelastic collision cross section. A limitation to this technique as generally

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[1] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, England, 1955).

[2] J. D. Craggs and H. S. W. Massey, in *Handbuch der Physik*, S. Flügge, Ed. (Springer-Verlag, Berlin, 1956), Vol. 37/1. See also the review by T. L. Cottrell and I. C. Walker, Quart. Rev. **20**, 153 (1966). The importance of rotational excitation in swarm experiments appears to have been first recognized by W. H. Bennett and L. H. Thomas, Phys. Rev. **62**, 41 (1942).

[3] Typical electron beam techniques are described by W. L. Fite, *Atomic and Molecular Processes*, D. R. Bates, Ed. (Academic Press Inc., New York, 1962), Chap. 12. Recently developed electrostatic analyzer techniques are described in Refs. 27 and 36. The application of the trapped electron technique to vibrational excitation is discussed in Ref. 41.

[4] H. Maier-Leibnitz, Z. Physik **95**, 499 (1935). Applications of this technique to the study of vibrational excitation are discussed in Refs. 29 and 35. A recent critique of the theory used in the analyses of such experiments is given in P. J. Chantry, A. V. Phelps, and G. J. Schulz, Phys. Rev. **152**, 81 (1966).

employed is that the minimum energy spread of the electrons is approximately 0.2 eV as determined by the hot filament used as an electron source. The minimum energy to which this technique has been applied is about 1.5 eV.

According to the electron swarm technique,[1,2,5,6] one determines the inelastic scattering cross sections from analyses of measured electron transport coefficients. These transport coefficients, e.g., the electron mobility and diffusion coefficient, characterize the motion of electrons as they drift through the gas under the influence of a uniform electric field and for a given field strength to gas density ratio are determined by rates of elastic and inelastic scattering of the electrons. In these experiments electrons are emitted from a cathode into a region of uniform electric field filled with gas at an appreciable fraction of an atmosphere. The electrons quickly come to an equilibrium in which the rate of gain of energy from the electric field and the rate loss of energy in collisions with the gas molecules are equal. One measures the electron drift velocity w from the time required for the electrons to cross the drift region. One can also measure the ratio of the electron diffusion coefficient D to the electron mobility μ from the lateral spread of the electrons as they cross the tube. The product of the D/μ ratio and the electronic charge has the dimensions of an energy and has been called[6] the characteristic energy ϵ_K. The characteristic energy is measurable whereas there are no presently available techniques for measuring the mean energy of the electrons under the conditions of these experiments. When the electron energy distribution function is Maxwellain, the characteristic energy is equal to the product of the Boltzmann constant k and the electron temperature T_e and is $\frac{2}{3}$ of the mean electron energy. The minimum characteristic electron energy is determined by the gas temperature and has been as low as 0.007 eV corresponding to kT at 77°K. The spread in electron energies and, therefore, the available energy resolution in electron swarm experiments in which the inelastic cross sections[7] vary slowly with energy is of the order of the average energy of the electrons, i.e., from 0.01 to several eV at mean energies of 0.01 and several eV. A considerable increase in effective energy resolution can occur at electron energies near the onset of a new class of energy-loss processes[8] or when the inelastic excitation cross section increases suddenly due to a resonance. Since the procedure for the determination of electron collision cross sections from transport coefficient data is relatively unfamiliar, it is reviewed in the Appendix.

The final class of experiments involves the measurement of the relaxation of electron energy using high-frequency techniques.[9] Free electrons are produced in the gas either by a pulsed discharge or by irradiation with a pulse of high-energy electrons. After the electrons produced by the discharge cool to the gas temperature, they are heated momentarily with a high-frequency disturbing pulse of moderate field strength. Following this pulse the electron energy again relaxes to the thermal equilibrium value. If the electron collision frequency varies with the electron energy, this relaxation time constant can be determined from the time variation of the attenuation of a weak microwave sensing signal. High rates of energy relaxation occur in gases with large rotational and vibrational excitation cross sections. Under favorable experimental conditions, e.g., high-electron densities, the radiation temperature of the electrons can be measured by comparison of the microwave noise generated by the decaying plasma with that of a calibrated noise source using a high sensitivity receiver. The energy resolution available with this technique is similar to that of the electron swarm techniques discussed above. Laboratory studies using this technique are relatively recent so that neither the experimental techniques nor the theoretical relations between observed quantities and excitation cross sections are as highly developed as for the techniques discussed above. At present this is the only technique which has yielded information regarding rotational excitation in gases for which electron attachment is rapid, e.g., O_2 and NO. Because of the large amount of energy deposited in the gas during the pulsed discharges considerable difficulty is often encountered in making energy relaxation measurements at the lower electron energies, i.e., below roughly 0.1 eV.

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[5] The experimental aspects of the electron swarm technique have been reviewed by L. G. H. Huxley and R. W. Crompton, in *Atomic and Molecular Processes*, D. R. Bates, Ed. (Academic Press Inc., New York, 1962), Chap. 10.

[6] The principles of the analysis of the transport coefficients in terms of inelastic collision cross sections are given by L. S. Frost and A. V. Phelps, Phys. Rev. **127**, 1621 (1962).

[7] Although the determination of elastic or momentum transfer cross sections from transport coefficient data is not the subject of this paper, it is of interest to note that this technique is highly sensitive to the presence of a minimum in the momentum transfer cross section because of the presence of this cross section in the denominator of the integrand of the theoretical expressions for the diffusion and mobility coefficients given in Eqs. (A1) and (A2) of the Appendix. This point is in direct contradiction to the claim of D. E. Golden, Phys. Rev. **151**, 48 (1966).

[8] An example of the use of this sensitivity is the determination of the cross section for the excitation of Cs near threshold by J. F. Nolan and A. V. Phelps, Phys. Rev. **140**, A792 (1965). This paper also illustrates the possibility of cross-section determination using measurements of only drift velocity in a mixture consisting of a small fraction of the molecular gas and a noble gas having a known momentum transfer cross section. See also A. G. Engelhardt and A. V. Phelps, Phys. Rev. **133**, A375 (1964).

[9] Experimental techniques used in microwave studies of electron relaxation are reviewed by V. E. Golant, Zh. Tekh. Fiz. **30**, 1265 (1960) [English transl.: Soviet Phys.—Tech. Phys. **5**, 1197 (1961)]. The general theory of such experiments is discussed by V. L. Ginsburg and A. V. Gurevich, Usp. Fiz. Nauk **70**, 201 and 393 (1960) [English transl.: Soviet Phys.—Uspekhi **3**, 147 and 175 (1960)]. The most accurate published theory of the role of inelastic collisions in these experiments is that of Ref. 22. Examples of the application of this technique are given in Refs. 22, 25, and 26.

In principle, energy relaxation data can be obtained for the molecules of air from ionospheric cross modulation experiments[9] when the air density is accurately known in the region of interaction.

The electron beam technique is easiest to understand and simplest to interpret of these experimental techniques. Also, the electron beam technique provides the only method capable of resolving the detailed structure of resonances observed in the total and inelastic cross sections. On the other hand, one must use the electron swarm or electron energy relaxation techniques in order to detect the smaller energy losses characteristic of rotational excitation in heavy gases. The electron swarm technique has the advantage that one can measure transport coefficients with a high degree of precision, e.g., less than 1%.

III. HOMONUCLEAR MOLECULES

A. Rotational Excitation of H_2, N_2, and O_2

We consider first the rotational excitation collisions involving homonuclear molecules, such as hydrogen, nitrogen, and oxygen. Figure 1 shows the results of theory and the cross sections derived from experiment for rotational excitation of hydrogen. Here are plotted the cross sections for rotational excitation of hydrogen molecules from the $J=0$ to $J=2$ level; that is, the lowest allowed transition for parahydrogen. The solid curves show the results of analyses by Engelhardt and Phelps[10] of electron swarm experiments. The differences in the two solid curves are a measure of the uncertainty in their result.[11] The accuracy to which these cross sections agree with experiment can best be seen by a comparison of calculated and measured transport coefficients, i.e., the inverted triangles and the solid curve for ν_u/N in Fig. 10 of the Appendix. The effect of the $J=1$ to $J=3$ transition must be included in the analysis of most experimental data since the ortho–parahydrogen ratio is usually that corresponding to 300°K.

The lowest broken curve in Fig. 1 shows the theoretical curve calculated by Gerjuoy and Stein[12] on the assumption that the only significant interaction is that due to the permanent electric quadrupole moment of the hydrogen molecule. Those earlier and recent calculations[13] which omit the quadrupole interaction yielded rotational excitation cross sections for H_2 which are much too small at electron energies for which experimental data on rotational excitation is available. Gerjuoy and Stein show that the Born approximation is expected to be more accurate as the electron energy is lowered. The next higher broken curve represents the effects of the addition of asymmetric polarization terms by Dalgarno and Moffett.[14] The upper two broken curves show the effect of inclusion of symmetric and asymmetric polarization terms by Sampson and Mjolsness[15] and of short-range terms by Geltman and Takayanagi.[16] These two calculations were carried out using a distorted wave technique and the adjustable parameters of the short-range cutoff of the polarization potential were chosen to give the best over-all fit to

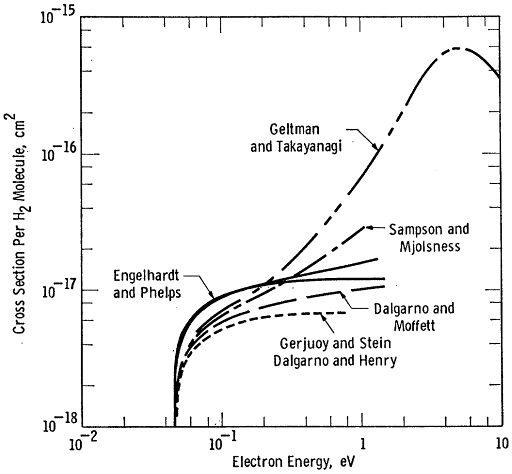

FIG 1. Cross section for rotational excitation of H_2 from the $J=0$ to the $J=2$ level. The solid curves are obtained by adjusting the effective quadrupole moment to obtain consistency with transport coefficient data. The broken curves are the results of various theoretical calculations discussed in the text. These cross sections must be multiplied by the fraction of H_2 molecules in the $J=0$ rotational state in order to obtain the corresponding Q of Eq. (A5) of the Appendix.

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[10] A. G. Engelhardt and A. V. Phelps, Phys. Rev. **131**, 2115 (1963). Note that the portion of this reference concerned with electronic excitation, i.e., $\epsilon_K > 2$ eV, needs to be modified to take into account the results of R. W. Crompton, B. S. Liley, A. I. McIntosh, and C. A. Hurst, in *Proceedings of the Seventh International Conference on Ionization Phenomena in Gases*, B. Perović and D. Tošić, Eds. (Gradevinska Knjiga Publishing House, Beograd, 1966), Vol. 1, p. 86; of P. A. Lawson and J. Lucas, Proc. Phys. Soc. (London) **85**, 177 (1965); and of J. Fletcher and S. C. Haydon, Australian J. Phys. **19**, 615 (1966). Also, the statistical weights assigned to the rotational levels of D_2 are incorrect so that the derived effective quadrupole moment for D_2 is only approximate. See Ref. 20.

[11] When the Dalgarno and Moffett cross section shown in Fig. 1 is used to calculate ν_u/N values of Fig. 10, the discrepancy between the calculated and experimental values of ν_u/N is 15%–20% for $0.04 < \epsilon_K < 0.1$ eV.

[12] E. Gerjouy and S. Stein, Phys. Rev. **97**, 1671 (1955); **98**, 1848 (1955).

[13] P. M. Morse, Phys. Rev. **90**, 51 (1953); T. R. Carson, Proc. Phys. Soc. (London) **A67**, 909 (1954); and Yu. D. Oksyuk, Zh. Eksperim. i Teor. Fiz. **49**, 1261 (1965) [English transl.: Soviet Phys.—JETP **22**, 873 (1966)].

[14] A. Dalgarno and R. J. Moffett, Proc. Natl. Acad. Sci. India **A33**, 511 (1963).

[15] D. H. Sampson and R. C. Mjolsness, Phys. Rev. **140**, A1466 (1965).

[16] S. Geltman and K. Takayanagi, Phys. Rev. **143**, 25 (1966); see also K. Takayanagi and T. Takahashi, Rept. Ionosphere Space Res. Japan **20**, 357 (1966).

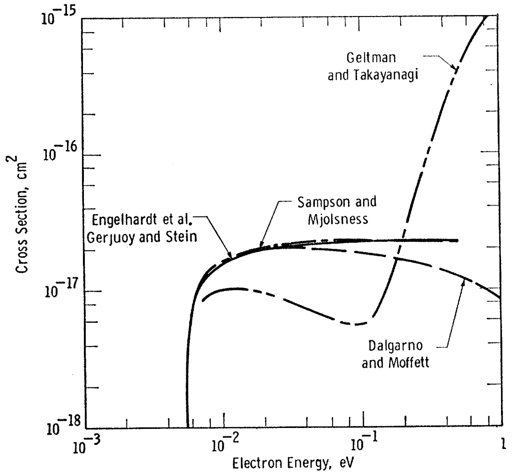

FIG. 2. Cross section for the rotational excitation of N_2 from the $J=4$ to the $J=6$ level. The solid curve was obtained by Engelhardt, Phelps, and Risk by adjusting the effective quadrupole moment of the theory of Gerjuoy and Stein to obtain consistency with the transport coefficient data. The broken curves show excitation cross sections given by other theoretical calculations using a quadrupole moment of $-1.10\ ea_0^2$. These cross sections must be multiplied by the fraction of the N_2 molecules in the initial $J=4$ rotational state in order to obtain the Q's of Eq. (A5) of the Appendix. Collisions of the second kind must be taken into account when comparing these cross sections with experiment.

elastic scattering data. Dalgarno and Henry[17] obtained results similar to those of Gerjuoy and Stein when they included short-range terms but no polarization terms. Recently, Lane and Geltman[18] have completed a close coupling calculation and obtained results which, for the energy range up to 1 eV, are similar to those of Sampson and Mjolsness. Lane and Geltman chose the polarization cutoff parameters to fit the elastic scattering data in the range of energies where the partial waves of greatest importance in the rotational excitation are of greatest importance in elastic scattering. Lane and Henry[19] have reported similar results using a polarized orbital calculation. Further comparisons between experiment and theory are currently being made by Crompton and McIntosh[20] using parahydrogen instead of a mixture of ortho and parahydrogen. Preliminary results indicate that the agreement between experiment and the theoretical cross section obtained by Lane and Geltman equals the sum of the combined experimental and computational errors.

In the case of nitrogen, the permanent electric quadrupole moment is larger than that of hydrogen. However, there are some 20 rotational states which must be taken into account even at liquid nitrogen temperatures. The net effect of this is to reduce the rate of energy exchange between electrons and nitrogen molecules due to rotational excitation collisions relative to the rate for electrons and hydrogen molecules. Because of the large number of rotational transitions which must be considered for heavy gases, it is convenient to make use of algebraic expressions which relate the various cross sections, e.g., the Gerjuoy–Stein or Dalgarno–Moffett formulas. One then adjusts one or two parameters for a best fit to the experimental data. The net effect of this procedure is that there is little sensitivity to the shape of the rotational excitation cross sections near the thresholds but that one can distinguish between various theories at higher energies. In the case of nitrogen, Engelhardt, Phelps, and Risk[21] found that using the theory of Gerjuoy and Stein[12] and an effective quadrupole moment of $1.04ea_0^2$, one obtains very good agreement between the experimental and theoretical transport coefficients. The fit to experiment obtained using the theory of Dalgarno and Moffett[14] was significantly poorer. Reasonable agreement between theory and experiment has also been found by Mentzoni and Row[22] from studies of the energy relaxation of electrons following a microwave heating pulse.

Figure 2 shows the rotational excitation cross section for N_2 calculated using the Gerjuoy and Stein formulas for a typical rotational transition, i.e., the $J=4$ to $J=6$ transition, and a quadrupole moment of $1.04ea_0^2$. For the same quadrupole moment Dalgarno and Moffett[14] predict a 40% lower rotational excitation cross section near 0.3 eV. However, using distorted wave calculations, Sampson and Mjolsness[15] have found a cross section which is only 5–15% lower than that of Gerjuoy and Stein for electron energies below about 0.5 eV. As indicated by the curves of Fig. 2 the use of the Sampson and Mjolsness correction to Gerjuoy and Stein gives good agreement with experiment using a quadrupole moment equal to the recently recommended value[23] of $1.10ea_0^2$. Figure 2 shows that Geltman and Takayanagi[16] predict much lower cross section at low energies and that at energies near 1 eV they predict a very large cross section. Although no attempt has been made to use their cross sections to calculate transport coefficients, it is almost certain that the differences between the calculated and experimental values will be rather large at energies near 0.07 and above 0.3 eV. A very large rotational excitation cross section near 2 eV has been also calculated theoretically

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[17] A. Dalgarno and R. J. W. Henry, Proc. Phys. Soc. (London) **85,** 679 (1965).

[18] N. F. Lane and S. Geltman, Phys. Rev. **160,** 53 (1967).

[19] N. F. Lane and R. J. W. Henry, Bull. Am. Phys. Soc. **12,** 177 (1967).

[20] R. W. Crompton and A. I. McIntosh, Phys. Rev. Letters, **18,** 527 (1967); and (private communication).

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

[22] M. H. Mentzoni and R. V. Row, Phys. Rev. **130,** 2312 (1963); see, also, V. A. J. van Lint, IEEE Trans. Nucl. Sci. **NS-11,** 266 (1964).

[23] D. E. Strogryn and A. P. Strogryn, Mol. Phys. **11,** 371 (1966).

by Oksyuk.[13] Chen[24] has calculated the effect of the resonance near 2 eV on the rotational excitation of N_2 at electron energies near the resonance. At present there are no experimental techniques capable of determining rotational excitation cross sections at electron energies above about 0.3 eV for gases other than H_2 and D_2.

In the case of oxygen, the electric quadrupole moment[23] is much smaller than that for hydrogen or nitrogen and it appears that the theory of Gerjuoy and Stein may not be applicable over a singificant energy range. In particular, Geltman and Takayanagi[16] suggest that the short range forces are dominant and that the cross section is a rapidly increasing function of electron energy at energies near 0.01 eV. Because of large electron attachment rates, present swarm techniques are not capable of measuring w and ϵ_K at low enough ϵ_K to allow accurate determinations of rotational excitation cross sections in O_2. However, Narasinga Rao and Goldstein[25] and Mentzoni and Narasinga Rao[26] have measured electron energy relaxation times corresponding to rather large rotational excitation cross sections.

B. Vibrational Excitation of H_2, N_2, and O_2

In this section we consider the vibrational excitation of homonuclear molecules. Figure 3 shows the results of some of the experimental and theoretical determinations of the cross sections for vibrational excitation of H_2. The energy required for excitation of the $v=0$ to $v=1$ transition is 0.52 eV. The solid curves marked Schulz show the cross sections for excitation of the $v=1$ and $v=2$ levels as calculated from measurements[27] of electron scattering at 72°. According to Bardsley, Herzenberg, and Mandl[28] these cross sections should be increased by a factor of 1.4 to correct for nonisotropic scattering of the electrons. The curve marked Ramien[29] shows the results of a multiple scattering experiment in which the sum of the cross sections for excitation of the $v=1$ and $v=2$ levels was determined. The results shown for Engelhardt and Phelps[10] were determined from an analysis of transport coefficient data. Since these authors assumed only the $v=1$ level cross section was significant, their derived cross section is too high at energies above about 1 eV by roughly twice the cross section for excitation of the $v=2$ level. We conclude that the three experimental determinations are reasonably consistent at electron energies above 1.5 eV. The apparent discrepancy between the electron drift results and the electron beam results in the energy range from 0.5 to 1 eV is significant because this is the region

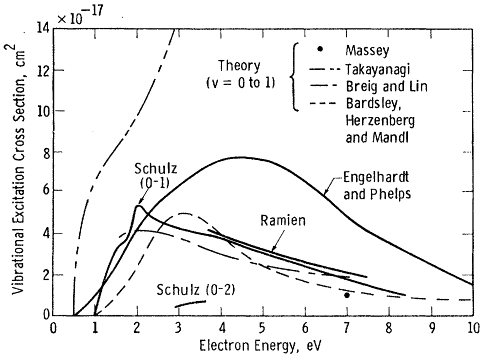

FIG. 3. Vibrational excitation cross sections for H_2. The solid curves are determined from experiment while the broken curves are the result of theoretical calculations.

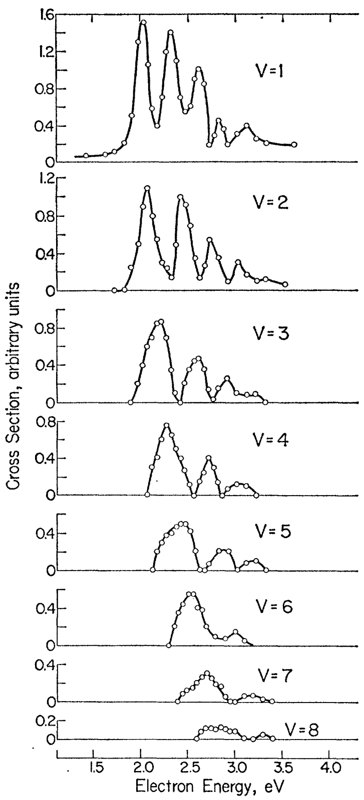

FIG. 4. Vibrational excitation of N_2 in the resonance region near 2 eV as measured by Schulz. The units of cross section are approximately 10^{-16} cm^2.

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[24] J. C. Y. Chen, Phys. Rev. **146**, 61 (1966).

[25] K. V. Narasinga Rao and L. Golstein, *Proceedings of the Sixth International Conference on Ionization Phenomena in Gases*, P. Hubert, Ed. (S.E.R.M.A., Paris, 1964), Vol. III, p. 69.

[26] M. H. Mentzoni and K. V. Narasinga Rao, Phys. Rev. Letters **14**, 779 (1965).

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

[28] J. N. Bardsley, A. Herzenberg, and F. Mandl, Proc. Phys. Soc. (London) **89**, 321 (1966).

[29] H. Ramien, Z. Physik **70**, 353 (1931).

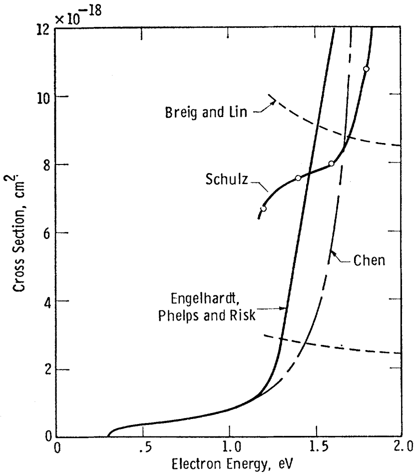

Fig. 5. Vibrational excitation in N_2 near threshold. The solid curves are determined from experiment and the broken curves are the results of theory.

of the highest sensitivity of the electron transport coefficient type of analysis. Recently, Menendez and Holt[30] have indicated that measurements of energy loss by electrons scattered through very small angles show a vibrational excitation cross section rising approximately linearly from threshold at about 0.5 eV as found from the transport coefficient analysis.

Many attempts to calculate theoretical vibrational excitation cross sections for H_2 yielded values[13,31] which were much smaller than experiment. Figure 3 shows only the results of the more successful calculations. A single point is shown for Massey.[32] In this calculation the effective nuclear charge was allowed to change with the internuclear separation. The results shown for Takayanagi[33] were calculated using a theoretical estimate of the variation in the symmetric portion of the polarization potential with internuclear separation and a short-range cutoff parameter for the polarization potential determined by fitting calculated and measured elastic scattering cross sections. Breig and Lin[34] used Raman intensity data to determine the variation in polarization with internuclear separation and investigated a number of approximations for the short-range cutoff of the polarization potential. The results of Breig and Lin suggest that the rather large cross section obtained by Takayanagi is due to the choice of polarization potential at distances close to the origin. A third type of calculation is represented by that of Bardsley, Herzenberg, and Mandl.[28] These authors assumed that the interaction between the electron and the hydrogen molecule could best be described in terms of a resonance between the electron and the molecular potential. According to this model an electron is first captured in a temporary negative ion state of the molecule. After a short time the electron escapes from the molecule and the molecule returns either to the ground state or to some excited state. The energy of the incident electron required to excite the molecule by this process is determined by the location of the resonance and may lead to an excitation cross section which shows a resonant peak of energies well above the threshold for excitation. In the case of H_2, the resonance is rather broad and peaks at an electron energy of about 3 eV. One success of the resonance approach is the calculation of a ratio for the excitation cross sections for the $v=1$ and $v=2$ levels in reasonable agreement with Schulz's experimental data. The curves shown here for Breig and Lin and for Bardsley, Herzenberg, and Mandl are the averages of curves shown by these authors for various values of the adjustable parameter of the theory. In summary, the theoretical calculations shown in Fig. 3 for hydrogen are in reasonable agreement with experiments, but further experimental and theoretical work is desirable.

An example of a situation in which the resonance character of vibrational excitation is obvious is that of the vibrational excitation of nitrogen in the vicinity of 2 eV. This mode of vibrational excitation was first discovered by Haas[35] and has been examined experimentally in great detail by Schulz.[27,36] Figure 4 shows cross sections for excitation of the first eight vibrational

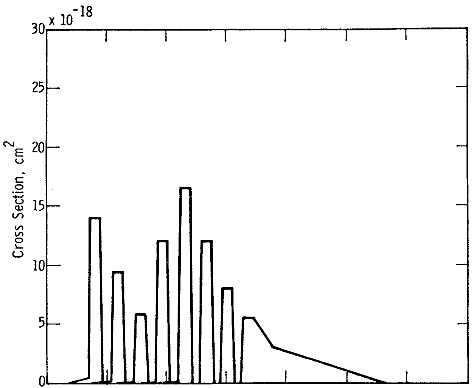

Fig. 6. Proposed vibrational excitation cross sections for O_2. The detailed shape of these resonances were chosen for computational convenience so that the area and the position in energy of the peaks are the significant features.

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[30] M. G. Menendez and H. K. Holt, J. Chem. Phys. **45**, 2743 (1966).

[31] T. Y. Wu, Phys. Rev. **71**, 111 (1947); see also J. C. Y. Chen and J. L. Magee, J. Chem. Phys. **36**, 1407 (1962).

[32] H. S. W. Massey, Trans. Faraday Soc. **31**, 556 (1935). Note, however, that an extension of this work by Carson (Ref. 13) yields significantly lower cross sections.

[33] K. Takayanagi, J. Phys. Soc. Japan **20**, 562 (1965).

[34] E. L. Breig and C. C. Lin, J. Chem. Phys. **43**, 3839 (1965).

[35] R. Haas, Z. Physik **148**, 177 (1957).

[36] G. J. Schulz, Phys. Rev. **116**, 1141 (1959); and **125**, 229 (1962); see also H. G. M. Heideman, C. E. Kuyatt, and G. E. Chamberlain, J. Chem. Phys. **44**, 355 (1966).

levels as measured by Schulz using electron beam techniques. Although the cross sections given are in arbitrary units, Schulz concludes that the units are approximately 10^{-16} cm^2. This means that the total vibration excitation cross section reaches approximately 5×10^{-16} cm^2 at about 2.2 eV. This result is consistent with the results of analyses of transport data.[21] In addition to the very large cross sections shown by this data, each of the cross-section curves contains a great deal of structure. This structure and the large cross section have led to the postulate that this is a good example of a case in which the electron molecule collisions should be described in terms of the resonance picture. Herzenberg and Mandl[37] and Chen[38] have fitted resonance theory to the experimental data with rather good results. Some discrepancies may remain[39] but the dominant features are satisfactorily described by this model.

The portion of the vibrational excitation curves for nitrogen near threshold is shown in greater detail in Fig. 5. The open circles represent the low-energy portion of the data obtained by Schulz.[36] The smooth solid curve labeled Engelhardt, Phelps, and Risk was obtained by analysis of electron drift experiments.[21] This curve illustrates the point that the electron swarm experiment analysis is capable of yielding results for low-magnitude cross sections at energies closer to threshold than is presently possible using the electron beam technique. At present we do not understand the apparent discrepancy between the electron beam results and the results of analysis of electron transport coefficient data. The theoretical curve shown for Chen[38] is actually the lower energy portion of the curve obtained by fitting resonance theory to the large resonance peaks shown in Fig. 4. For energies below 1 eV one obtains very good agreement between the results of transport coefficient analysis and cross section postulated by Chen. Some of the apparent discrepancy at energies near 1.5 eV may be due to the fact that the possibility of excitation of vibration states with $v > 1$ was neglected in the analysis of transport coefficient data[21] for energies below 1.7 eV. The short dashed curves shown for Breig and Lin[34] represent limiting calculations by these authors based on a model of a nitrogen molecule with an approximate polarization interaction which varies with internuclear separation. The variation in polarization with internuclear potential was determined from Raman intensity measurements. This theory does not predict the very large cross sections at energies of the order of 2 eV and appears to yield much too large a cross section for electron energies approaching threshold.

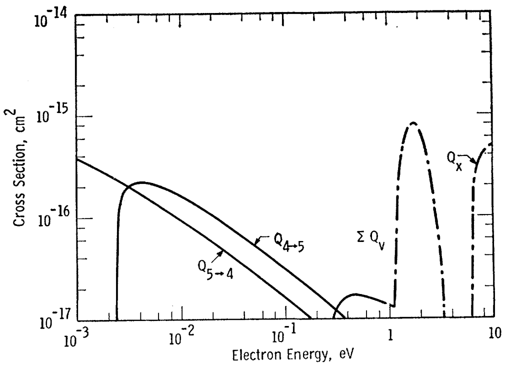

FIG. 7. Rotational and vibrational excitation cross sections for CO. The solid curves were obtained by adjusting the effective electric dipole moment and infrared transition probability so as to obtain consistency with transport coefficient data as discussed in the text. The broken curve is the sum of the vibrational excitation cross sections measured by Schulz.

In view of the success of the resonance picture in N_2, CO [36] and N_2O,[40] Schulz and Dowell[41] postulate resonance behavior in oxygen where there is no direct evidence for resonances but where there is a need for a large vibrational excitation cross section to explain the transport coefficient data.[2,42] This series of resonances is expected to occur at the vibrational states of the oxygen negative ion. Figure 6 shows the cross sections which are proposed by Hake and Phelps[42] to explain the various experimental data obtained for oxygen. First, the electron transport coefficient data[42] shows that the vibrational excitation cross sections in oxygen are quite large, e.g., much larger than for N_2 for $0.1 < \epsilon_K < 0.8$ eV. Second, the electron beam data of Schulz and Dowell using a trapped electron technique[41] indicates that the vibrational excitation cross sections in oxygen near threshold are small. Third, there is the observation by Schulz[43] of structure in the three-body attachment coefficient curve for formation of O_2^- molecules. Finally, Boness and Hasted[44] observe a series of resonance-like peaks in the total scattering cross section in the energy range from a few tenths of an electron volt to about 1 eV. The resonance peaks shown in Fig. 6 are a first attempt to find a set of cross sections

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[37] A. Herzenberg and F. Mandl, Proc. Roy. Soc. (London) **A270**, 48 (1962).

[38] J. C. Y. Chen, J. Chem. Phys. **40**, 3507 (1964); **45**, 2710 (1966); and Phys. Letters **8**, 183 (1964).

[39] Measurements of total (elastic plus inelastic) scattering cross sections for N_2 by Golden have shown a series of lower magnitude resonances at energies between 0.3 and 1.7 eV which are not included in the models which have been used to fit N_2 data. See D. E. Golden, Phys. Rev. Letters **17**, 847 (1966). However, more recent experiments fail to show these resonances. See H. Ehrhardt and K. Willmann, *Proceedings of the 5th International Conference on Electronic and Atomic Collisions* (Publishing House Nauka, Leningrad, 1967), p. 486. Also, Schulz (Ref. 36) obtained evidence for what appears to be a significant (Ref. 21) vibrational excitation process in N_2 at electron energies near 5 eV.

[40] G. J. Schulz, J. Chem. Phys. **34**, 1778 (1961).

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

[42] R. D. Hake, Jr. and A. V. Phelps, Phys. Rev. **158**, 70 (1967).

[43] G. J. Schulz, Bull. Am. Phys. Soc. **6**, 387 (1962).

[44] M. J. W. Boness and J. B. Hasted, Phys. Letters **21**, 526 (1966).

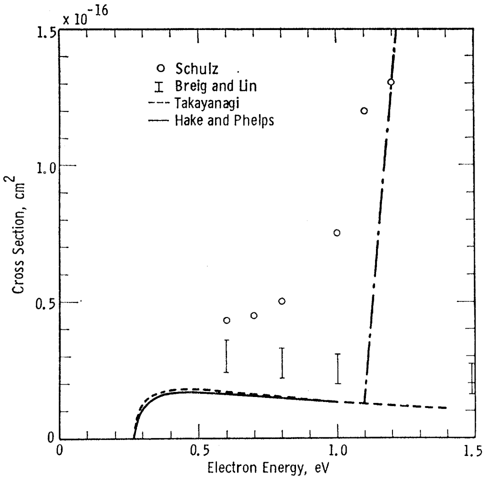

FIG. 8. Vibrational excitation cross sections for CO near threshold. The solid curve was obtained by adjusting the effective infrared transition probability to obtain consistency with transport coefficient data as discussed in the text. The open points are the results of measurements of electron scattering at 72° by Schulz. The vertical error bars and the short dashed curve are the results of threotical calculations discussed in the text.

which are consistent with all of these experiments. In particular, since these cross sections are chosen to be consistent with the electron drift tube data, they should be useful for calculation of transport coefficient and of gross vibrational excitation rates. The rising peak values for the cross sections above about 1 eV may very well indicate[41,42] the onset of excitation of the $a^1\Delta_g$ level of the oxygen molecule rather than vibrational excitation as shown in Fig. 6.

IV. HETERONUCLEAR MOLECULES

A. Rotational Excitation

The first heteronuclear molecule which is considered here is CO. Figure 7 shows the cross sections for rotational excitation from the $J=4$ to the $J=5$ level and for rotational de-excitation from the $J=5$ level to the $J=4$ level. In this case the selection rule is $\Delta J=\pm 1$, since the dominant interaction is due to the electric dipole moment of the molecule. The cross sections shown here were calculated using formulas obtained by Takayanagi[45] using the Born approximation and a molecular potential consisting only of the permanent dipole moment. Hake and Phelps[42] used a recent value of the dipole moment[46] for CO and found that when all of the various rotational excitation cross sections, there being about 20 of them, are included in the Boltzmann equation there is very good agreement between the experimental and calculated electron transport coefficients. The rotational excitation cross section shown in Fig. 7 has a behavior typical of an allowed dipole transition, i.e., it decreases as ϵ^{-1} ln (ϵ) at high energies. This same theoretical cross section for rotational excitation has been used in analyses[47] of H_2O and NO in both cases seems to give reasonable agreement with the small amount of available experimental data.[48] The effect of rotational excitation due to the electric quadrupole moment, $\Delta J=\pm 2$, is expected to be small[12,42] at energies below the onset of vibrational excitation for gases with dipole moments as large as that for CO.

B. Vibrational Excitation of CO

Figure 7 also shows the sum of the vibrational excitation cross sections for the CO molecule. There are two distinct regions. For energies above 1 eV there is a very large resonance similar to that found in N_2. This resonance has been discussed in detail by Schulz.[36] At electron energies near threshold we see that although the cross section is much smaller than at the peak of the resonance, it is about a factor of fifty larger than for N_2 near threshold.

The details of the threshold region of the vibrational excitation cross section for CO are shown in Fig. 8. Here the results of the cross section determination using electron transport coefficient data[42] are shown by the solid curve. The short dashed curve is the cross section calculated using a formula given by Takayanagi[45] in which the Born approximation is used and in which the only parameter required is the infrared transition probability. Using the value for the transition probability given by Penner[49] one finds very good agreement between the theoretical cross section and that determined from analyses of transport coefficient data. The vertical error bars indicate the range of calculated cross sections obtained by Breig and Lin,[34] who included various approximate polarization potentials in their Born approximation calculation. While the agreement obtained without polarization may be fortuitous,[45] these results suggest that the effects of the polarization potential, i.e., distortion of the molecule, may be largely cancelled by distortion of the incident

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[45] K. Takayanagi, J. Phys. Soc. Japan **21**, 507 (1966). Earlier theoretical calculations for polar molecules are discussed in this reference. See also Ref. 34.

[46] C. A. Burrus, J. Chem. Phys. **28**, 427 (1958).

[47] A. V. Phelps and R. S. Cohen (unpublished). Note that some information on the relative cross sections for excitation of the $v=1$ and $v=2$ levels of NO is available from the experiments of A. B. Callear, J. A. Green, and G. J. Williams, Trans. Faraday Soc. **61**, 1831 (1965).

[48] For H_2O, only electron drift velocity data are available at low electron energies. See for example J. J. Lowke and J. A. Rees, Australian J. Phys. **16**, 447 (1963). For NO the only low-energy data are from energy relaxation experiments by K. V. Narasinga Rao and R. L. Taylor, Bull. Am. Phys. Soc. **12**, 810 (1967).

[49] S. S. Penner, *Quantitative Molecular Spectroscopy and Gas Emissitivities* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1959), p. 23.

electron wave function as appears to be the case in the calculation[15] of rotational excitation in N_2. The open circles show the low-energy results obtained by Schulz[36] using the double electrostatic analyzer for electron beam measurements. The almost vertical broken line represents a first approximation to the resonance structure which would be necessary to fit the electron swarm results. Unfortunately, there is no recent experimental transport coefficient data for CO at mean electron energies above 1.0 eV so that a more accurate analysis of the resonance region is not possible.

In summary, in the case of CO it appears that vibrational excitation occurs by two very distinct processes. Near threshold the vibrational excitation occurs through the dipole matrix element which also leads to infrared radiation. At higher energies there is a resonance of the electron with the CO molecule which leads to very large cross sections for vibrational excitation.

C. Vibrational Excitation of CO_2

Figure 9 shows the cross sections which Hake and Phelps[42] derive for the dominant vibrational excitation processes for CO_2, i.e., a set of four resonances, two of which have high-energy tails. The resonances at 0.3, 0.6, and 0.9 eV have been observed by Schulz[50] using electron beam techniques, as has the high energy tail for the 0.3 eV energy-loss process. Starting with the location of these resonances and with the transport coefficient data available in CO_2, the analysis of transport coefficient data leads one to conclude that there must be an additional resonance very close to the onset of vibrational excitation at 0.08 eV. The high-energy tails shown for the 0.08-eV process and the 0.3-eV energy-loss process were calculated using the theory of vibrational excitation given by Takayanagi[45] and, as discussed above, found[42] to be so successful for CO. The transition probability used for the 0.08 eV process was taken to be equal to that determined by infrared studies.[49] In the case of the 0.3 eV process it was necessary to take a cross section equal to 75% of that calculated using the infrared transition probability.[49] The excitation of the 0.08 eV process can only be associated with the bending mode of the CO_2 molecule. Hake and Phelps[42] point out that it is tempting to associate the 0.3-, 0.6-, and 0.9-eV energy loss processes with the three lowest levels of the asymmetric stretching mode of the CO_2 molecule since the progression in energy is in good agreement with the spectroscopic data.

A number of features of the results for CO_2 are not understood. Thus, it appears that the resonances in each case occur very close to the threshold for the onset of the particular energy loss process. This is quite different from the situation which is observed in H_2, N_2, and CO where the resonances occur well above threshold. Secondly, the presence of compound states or temporary negative ion states of the linear CO_2 molecule at very low energies (0.08 eV) suggests that there might very well be stable negative ion states of the CO_2 molecule in a bent configuration.[51] Electron attachment experiments[52] in CO_2 have failed to disclose any evidence for stable CO_2^-. Finally, the possible contribution of the apparent resonance for electrons of about 4 eV in CO_2 to vibrational or electronic excitation is unknown. This resonance has been observed only in the total scattering cross section, where it appears[44] to be similar to the resonance at 2 eV in N_2.

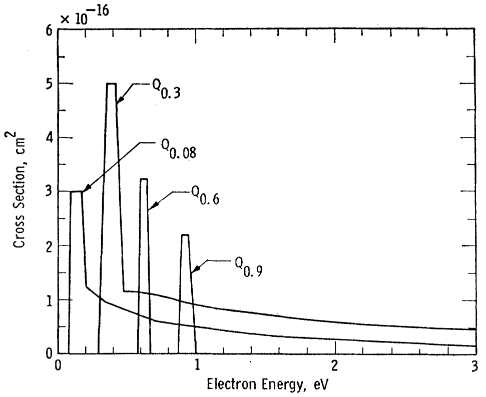

FIG. 9. Cross sections for vibrational excitation of CO_2 by electron impact. The subscripts to the Q's are the energy losses in eV associated with the various cross sections. The detailed shapes of the resonance portions of these curves were chosen for computational convenience so that the initial rise of the $Q_{0.08}$, the areas of all curves, and the location of the peaks in energy are the significant features of the resonances.

D. Vibrational Excitation of Other Gases

Evidence in favor of a series of resonances in NO, similar to those for O_2, has been obtained by Boness and Hasted[44] in their studies of the low-energy total scattering cross section for electrons. A preliminary analysis of NO has been made[47] on this assumption. In the case of NO one also has the possibility of vibrational excitation by the dipole transition moment which is not possible in the case of O_2.

In principle, the techniques discussed above could be applied to the analysis of data obtained for almost any molecular gas. As the complexity of the molecular gas increases the lack of uniqueness of the results becomes more serious. It is, however, interesting to speculate concerning the case of methane. Cottrell and

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[50] G. J. Schulz (unpublished).

[51] J. A. Pople and G. A. Segal, J. Chem. Phys. **44**, 3289 (1966); see also E. E. Ferguson, F. C. Feshenfeld, and A. L. Schmeltekopf, J. Chem. Phys. **47**, 3085 (1967).

[52] J. L. Pack and A. V. Phelps, J. Chem. Phys. **45**, 4316 (1966).

Walker[53] have measured very large values for the fractional energy loss per collision for CH_4, i.e., the ratio ν_u/ν_m defined in the Appendix is approximately 0.3 at energies rather close to the vibrational threshold. By considering the variation in ν_u/N and ν_m/N with characteristic energy ϵ_K, one readily sees that the maximum in the vibrational excitation cross section essentially coincides with the minimum in the momentum transfer cross section. Because of the similarity of CH_4 to the closed-shell structure of the rare gases, the minimum in the momentum transfer cross section has been interpreted as being due to a Ramsauer minimum.[1] It remains to be seen whether the close coincidence of the very large vibrational cross section and the Ramsauer minimum is accidental or not.[54] The coincidence will also complicate the analysis of swarm data using the Boltzmann transport data.[6,42] Another interesting property of methane is the absence of dipole and quadrupole moments so that rotational excitation can occur only via short-range forces and by octopole and higher moments. For this reason the rate of energy loss by low-energy electrons in CH_4 may be very small for $\epsilon_K<0.1$ eV and this gas may be a poor thermalizing gas for low-energy electrons. Measurements of w and ϵ_K at low ϵ_K would be necessary to test this possibility.

Cottrell and Walker[53] have also found very large fractional energy losses in gases such as SiH_4, SiD_4, C_2H_4, and N_2O. Although no detailed analyses have been carried out, the low values of ϵ_K at which these effects are observed leads one to expect that the energy loss is due primarily to vibrational excitation of these molecules. Large energy losses at low-electron energies in more complicated molecules have been observed using electron beam techniques by Bowman and Miller[55] and by Compton, Christophorou, and Huebner.[56] In several of these cases the authors propose that the excitation occurs through a resonance and results in vibrational excitation of the molecule.

V. SUMMARY

Considerable progress has been made in determining cross sections for rotational and vibrational excitation of simple molecules by low-energy electrons from experiment. Also, theories have been developed which are capable of explaining the major features of many of the results. Thus, simple theory shows very good agreement with experiment for the rotational excitation of N_2 and CO and shows agreement to within the accuracy of the experimental data for rotational excitation of NO and H_2O. It is not yet clear whether a significant discrepancy exists between experiment and theories for the rotational excitation of H_2. Born approximation calculations using only the dipole moment of the molecule predict accurately the vibrational excitation observed near threshold in CO. Resonance theory shows reasonable agreement with experiment for the vibrational excitation of the $v=1$ and $v=2$ levels of H_2. Resonance theory appears to be necessary to explain the very large vibrational excitation cross sections observed in gases such as N_2, CO, and CO_2. As yet the theory cannot predict these resonances from the molecular potentials in gases other than H_2.

Recent electron beam, electron, swarm and cross modulation experiments have yielded much additional information regarding the elastic scattering of electrons by molecules. Unfortunately, in recent years there has been much less effort devoted to the question of theoretical calculation of elastic scattering cross sections for molecules.

ACKNOWLEDGMENTS

The author acknowledges helpful discussions with many people, especially G. J. Schulz, P. J. Chantry, A. Herzenberg, and E. Gerjuoy.

APPENDIX: CROSS-SECTION DETERMINATION FROM TRANSPORT COEFFICIENTS

In this appendix we review the procedure[6,10,21,42] by which one obtains cross sections from measurements from measured electron transport coefficients. Equations (A1) through (A4) give the transport coefficients which characterize the results of electron swarm measurements. First, there is the electron mobility μ which is defined in Eq. (A1) as the electron drift velocity w divided by the electric field strength E. Thus,

$$\mu N \equiv \frac{w}{E/N} = (e/3m)\langle (1/v^2)(d/dv)(v^2/Q_m)\rangle. \tag{A1}$$

The mobility is multiplied by the gas density N so as to obtain a quantity which is independent of gas density at constant ratio of electric field strength to gas density. The electron mobility coefficient can also be calculated from the kinetic theory of electrons in gases,[57] using the expression on the right hand side of Eq. (A1). Here e and m are the electronic charge and

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[53] T. L. Cottrell and I. C. Walker, Trans. Faraday Soc. **61**, 1585 (1965).

[54] The author acknowledges discussion of this point with A. Herzenberg and G. J. Schulz.

[55] C. R. Bowman and W. D. Miller, J. Chem. Phys. **42**, 681 (1965).

[56] R. N. Crompton, L. G. Christophorou, and R. H. Heubner, Phys. Letters **23**, 656 (1966).

[57] The theory appropriate to the motion of electrons in gases under the conditions of swarm experiments is discussed in Ref. 6. For more general discussions see, for example, T. Holstein, Phys. Rev. **70**, 367 (1946); and W. P. Allis, in *Handbuch der Physik*, S. Flügge, Ed. (Springer-Verlag, Berlin, 1967), Vol. 21, p. 383. The accuracy of the assumed solutions of the Boltzmann equation for ϵ_K measurements is discussed by J. H. Parker, Jr., Phys. Rev. **132**, 2096 (1963).

mass. The brackets indicate an average over the electron velocity distribution function of an expression involving the electron speed v and the cross section for momentum transfer collisions Q_m. The cross section for momentum transfer collisions[1] involves a preferential weighting of those events in which the electron is scattered through angles approaching 180°.

The second transport coefficient considered in this discussion is the characteristic energy ϵ_K defined by the first equality in Eq. (A2).

$$\epsilon_K = eD/\mu = (e/3\mu N)\langle v/Q_m\rangle. \qquad \text{(A2)}$$

Here D is the electron diffusion coefficient. This quantity can be obtained experimentally by measuring the spread in the electrons as they move under the action of a uniform electric field in a drift tube.[5] This quantity can also be calculated from theory as indicated on the right-hand side of Eq. (A2) using an average over the electron velocity distribution of the reciprocal of the cross section for momentum transfer collisions.

The two transport coefficients, w and ϵ_K, could serve as a basis for a determination of electron scattering cross sections. However, it is more convenient to analyze data using transport coefficients which allow one to separate the effects of elastic and inelastic collisions. This has been accomplished by the introduction of two transport coefficients[6] defined by Eqs. (A3) and (A4). First, the momentum transfer collision frequency per molecule, ν_m/N, is defined as the electron charge divided by the product of the electron mass, the electron mobility and the gas density, i.e.,

$$\nu_m/N = e/m\mu N. \qquad \text{(A3)}$$

Since Eq. (A1) shows that μN is inversely proportional to a function of Q_m, we expect[7] ν_m/N to be proportional to the magnitude of Q_m. When plotted as a function of the characteristic energy, ν_m/N is found to be nearly independent of the details of the electron velocity distribution function for gases in which $Q_m(\epsilon)$ and the inelastic collision cross sections do not vary too rapidly with electron energy.[6,58]

Finally, the electron energy exchange frequency per molecule ν_u/N is defined in Eq. (A4) as the ratio of the product of the electron drift velocity, electronic charge, and the electric field strength to gas density ratio divided by the difference between the characteristic energy and kT. Thus,

$$\nu_u/N = we(E/N)/(\epsilon_K - kT). \qquad \text{(A4)}$$

The quantity ν_u is therefore the ratio of the power input per electron to the excess energy of the electron over its thermal value. Since the power input is equal to the rate of energy loss, ν_u is a measure of the frequency of collisions in which electrons lose their excess energy. For gases in which the inelastic cross sections do not vary too rapidly with electron energy, one finds[6,10,21,42] that ν_u/N is a good measure of the cross sections for inelastic collisions.

The transport coefficients are related to the cross sections from electron scattering through the electron energy distribution $f(\epsilon)$. The electron distribution function is related to the various cross sections through the differential-difference equation,

$$\begin{aligned}&\tfrac{1}{3}e^2(E/N)^2(d/d\epsilon)\{[\epsilon/NQ_m(\epsilon)][df(\epsilon)/d\epsilon]\}\\ &\quad+(2m/M)(d/d\epsilon)(\epsilon^2Q_m(\epsilon)\{f(\epsilon)+kT[df(\epsilon)/d\epsilon]\})\\ &\quad+\sum_j[(\epsilon+\epsilon_j)f(\epsilon+\epsilon_j)Q_j(\epsilon+\epsilon_j)-\epsilon f(\epsilon)Q_j(\epsilon)]\\ &\quad+\sum_j[(\epsilon-\epsilon_j)f(\epsilon-\epsilon_j)Q_{-j}(\epsilon-\epsilon_j)-\epsilon f(\epsilon)Q_{-j}(\epsilon)]=0.\end{aligned} \qquad \text{(A5)}$$

This equation is called the Boltzmann equation[57] and in the form given is appropriate to the behavior of low and moderate energy electrons in a uniform *dc* electric field. Rather than go into detail we simply cite the role of the various terms. The first term represents the effect of energy input to the electrons. It is proportional to the square of the ratio of the electric field strength to the gas density and is essentially a diffusion in energy space. The second term gives the net effect of energy loss due to recoil of the molecule in elastic collisions between electrons and molecules. This term is proportional to the ratio of the electron mass to the molecular mass and is negligible compared to the terms due to inelastic collisions in most molecular gases. Exceptions are hydrogen and deuterium and possibly methane. The third term gives the net effect of inelastic collisions in which electrons lose energy; that is, electrons of energy ϵ collide with a molecule and lose an energy ϵ_j. The cross section for this process is Q_j. The fourth term gives the effect of inelastic collisions of the second kind, i.e., collisions in which an electron of energy ϵ collides with a molecule and gains an energy ϵ_j. The cross section for these collisions is Q_{-j} and is related to Q_j through the principle of detailed balancing.[1,6]

The procedure which is used to determine the cross sections for elastic and inelastic scattering is to assume a set of approximate cross sections based on any available information; to substitute these cross sections into Eq. (A5); and to solve this equation on a high-speed digital computer for the electron energy distribution function. This distribution function is then used with the momentum transfer cross section to calculate the transport coefficients given in Eqs. (A1) through (A4). The momentum transfer and energy exchange frequencies are then compared with values calculated from experiment. On the basis of the discrepancies between these two values, the elastic and

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[58] A. E. D. Heylen, Proc. Phys. Soc. (London) **79**, 284 (1962).

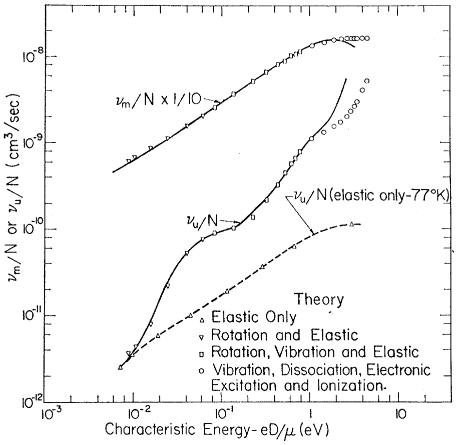

Fig. 10. Momentum transfer and energy exchange collision frequencies for H_2 at 77°K. The smooth curves are calculated from smooth curves through selected experimental data. The values indicated by the points are calculated using numerical solutions of the Boltzmann equation and the energy-loss process indicated in the legend.

inelastic cross sections are adjusted, the electron energy distribution function and the transport coefficients are recalculated, and a comparison is made again of calculated and experimental ν_m/N and ν_u/N values. This procedure is repeated until we obtain an agreement between calculated and experimental transport coefficients which is comparable for the accuracy of the experimental data.

The results of the procedure for determining cross sections from transport coefficients is illustrated by considering data appropriate to molecular hydrogen[6,10] as shown in Fig. 10. Here momentum transfer and energy exchange frequencies are plotted as a function of the characteristic energy of the electrons. The upper curve and points give the results of measurements and calculations of the momentum transfer collision frequency per molecule. This curve is not of interest in the best present discussion although it is generally best and sometimes essential,[42] to adjust the momentum transfer cross section to obtain a good fit to the ν_m/N curve as one adjusts the inelastic cross sections to fit the ν_u/N curve. The two lower curves give the energy exchange collision frequencies per molecule as calculated for various assumed cross sections and various energy loss processes. The lowest curve, which is shown broken, is calculated on the assumption that the only important energy loss is that due to recoil of the hydrogen molecule in elastic collisions between the electrons and the molecules. Under this assumption the two summation terms in Eq. (A5) are zero and Eq. (A5) can be integrated to obtain an integral expression[6,57] for $f(\epsilon)$. The solid smooth curve is calculated from an average of the best available experimental data. At very low characteristic energies, $\epsilon_K < 0.01$ eV, the only energy loss of importance is that due to elastic recoil of the molecules. However, at ϵ_K of about 0.01 eV a discrepancy between the two curves indicates the onset of a new energy-loss process. The only process which can occur at these low electron energies is that of excitation of the $J=2$ rotational level with a threshold at 0.045 eV. Using cross sections for the various $\Delta J=2$ transitions which were discussed in Sec. III, one calculates the values of ν_u/N shown by the inverted triangles and obtains good agreement with experiment. These rotational excitation cross sections fit the experimental data up to a characteristic energy of about 0.2 eV.

At characteristic energies above 0.2 eV a new inelastic process sets in. The most likely processes is vibrational excitation with a threshold at 0.52 eV. The square points show the fit to the experimental data (solid curve) which can be obtained by adjusting the vibrational excitation cross section to that given in Fig. 3. The additional rise in the energy exchange collision frequency at energies above about 2 eV is due to various electronic excitation processes.[10] We are not concerned with electronic excitation processes in this paper.

The analysis represented by the data of Fig. 10 for H_2 shows that the calculated energy exchange collision frequencies are directly proportional to the inelastic cross sections. If a single energy-loss process is dominant, one can determine its cross section to within the accuracy of the data; in the case of H_2 to about ±10% for the data considered in Ref. 10. As the accuracy of the data improves[20] the accuracy of the cross-section determination will increase. In Sects. III and IV of this paper, we have made our comparison between theory and swarm experiments in terms of cross sections because of the large number of theoretical cross sections and because of the possibility of comparison with beam experiment. However, the final judgment of the consistency of the theoretical cross section should be made by comparing calculated and measured transport coefficients[6,10,21,42] as in Fig. 10.