

## Vibrational Excitation of $N_2$ , CO, and $H_2$ by Electron Impact\*

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The cross section for vibrational excitation of  $N_2$ , CO, and  $H_2$  by electron impact is measured using a double electrostatic analyzer. Electrons are examined after scattering from the molecules at an angle of 72 deg. Both  $N_2$  and CO exhibit a small vibrational cross section to the first state below 1.7 and 1.0 eV, respectively, which is attributed to direct excitation by electron impact. Above these energies, many vibrational states are excited and the cross section becomes large; it is postulated that the excitation proceeds via a compound state of  $N_2$  and CO. The peak of the cross section occurs at 2.3 eV in  $N_2$  and 1.75 eV in CO. In hydrogen, the cross section to the first vibrational state predominates; the cross section to the second vibrational state of  $H_2$  is about 14% of the first state, at an energy of 3.4 eV.

THE vibrational excitation of nitrogen molecules by electron impact has been recently studied using a double electrostatic analyzer.<sup>1</sup> In that experiment, to be referred to as Part I, the forward scattered electrons were analyzed for energy losses, and it was found that the vibrational cross section is large in the energy range between 1.7 and 3.5 eV; that many vibrational levels become excited in this energy range; and that the cross section for excitation to individual vibrational states exhibits structure. These results confirm and extend two previous experiments on the vibrational cross section in nitrogen.<sup>2,3</sup> The results of part I were interpreted in terms of the existence of a temporary negative ion state,  $N_2^-$ . This temporary negative ion state is believed to provide the mechanism for the large observed cross section, the delayed onset of vibrational excitation, and for the oscillatory nature of the energy dependence of the individual cross sections.

Earlier theoretical treatments on vibrational excitation by electron impact have been confined to the hydrogen molecule,<sup>4</sup> but could not account for the large vibrational cross section observed in hydrogen. Recently, however, the vibrational cross section in nitrogen has also become the subject of theoretical discussion,<sup>5,6</sup> in which the theory of the compound state, developed previously for nuclear resonances, is used for the interpretation of the vibrational cross section.

The present experiment was undertaken in order to provide further experimental evidence for the vibrational cross section behavior in nitrogen and to extend the experimental technique to two other molecules.

The experiment of part I had two deficiencies; namely, (a) the elastically scattered electrons could not be distinguished from the primary beam since there is essentially no energy loss connected with the elastic-

ally scattered electrons, and (b) the cross section to the first vibrational level,  $v=1$ , could not be measured because the residual background current from the primary beam was too high. Both these deficiencies are associated with the fact that electrons were analyzed in the forward direction. The present experiment overcomes both these deficiencies by analyzing electrons at another angle, which is arbitrarily chosen as 72 deg. Also, it seemed desirable to substantiate by means of an experiment at another angle the basic conclusions resulting from the experiment of part I—namely, that a compound state of the molecule is consistent with the observed vibrational excitation.

### I. DOUBLE ELECTROSTATIC ANALYZER

The dimensions of the electrostatic analyzers used in part I have been preserved, but the geometry of the collision chamber has been altered. Figure 1 shows a

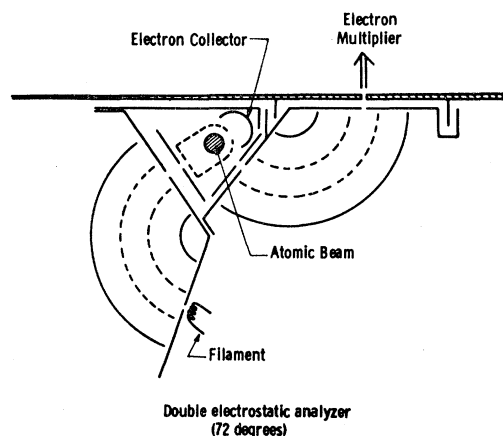


FIG. 1. Schematic diagram of double electrostatic analyzer. Electrons are emitted from the thoriated iridium filament. They pass between the cylindrical grids at an energy about 1.5 eV, and are accelerated into the collision chamber where they are crossed with a molecular beam. Those electrons scattered into the acceptance angle of the second electrostatic analyzer pass between the cylindrical grids, again at an energy approximately 1.5 eV. The electrons pass the exit slit into the second chamber (see Fig. 2) and impinge onto an electron multiplier. The shields are operated at lower voltages than in part I, i.e., about 5 V positive with respect to the 127-deg sections.

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<sup>1</sup> G. J. Schulz, Phys. Rev. **125**, 229 (1962).

<sup>2</sup> R. Haas, Z. Physik **148**, 177 (1957).

<sup>3</sup> G. J. Schulz, Phys. Rev. **116**, 1141 (1959).

<sup>4</sup> For a review, see J. D. Craggs and H. S. W. Massey, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1959), Vol. 37, p. 314.

<sup>5</sup> A. Herzenberg and F. Mandl, Proc. Roy. Soc. (London) **A270**, 48 (1962).

<sup>6</sup> J. C. Y. Chen, J. Chem. Phys. (to be published).

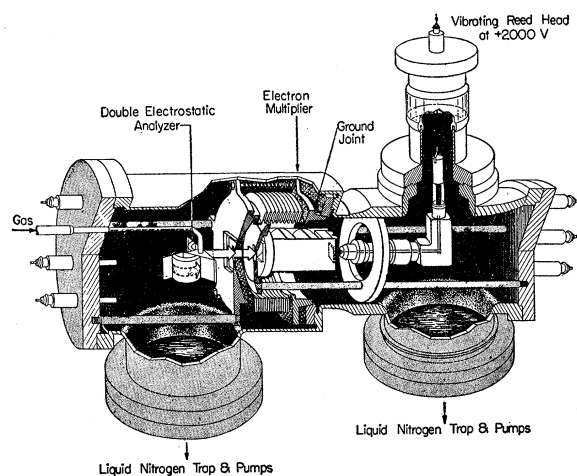


FIG. 2. Schematic diagram of vacuum envelope housing double electrostatic analyzer. The envelope is made of 304 stainless steel and assembled using gold gaskets. The double electrostatic analyzer (shown only schematically) is mounted on the plate carrying the slit. This plate, together with the bellows and the left-hand portion of the ground joint is inserted from the left, the multiplier assembly is inserted from the right, and the lead to the final dynode of the electron multiplier is brought out from the top. The head of the multiplier, inverted, is mounted on the top of the tube.

schematic diagram of the apparatus. Electrons emitted from a thorium-coated iridium filament traverse the first electrostatic analyzer at an energy 1.5 to 2.0 eV, and are focused by the entrance electrode near the collision chamber. The electron beam is crossed by a molecular beam in an equipotential region formed by gold-plated, tungsten grids. The electron collector collects the primary electron beam, maintained around  $10^{-9}$  A. Those electrons scattered around an angle of 72 deg are accepted by the second electrostatic analyzer, which is identical in dimensions to the first one. Normally, the second electrostatic analyzer is tuned to an electron energy identical to that of the first analyzer. Electrons passing the exit slit of the second electrostatic analyzer impinge on the first dynode of a ten-stage multiplier (DuMont 6292). A voltage of 1000 to 2000 V is applied to the multiplier. The last dynode (collector) of the multiplier is removed from the commercial unit and a well-insulated collector is substituted. This enables us to measure small currents at the output of the multiplier and thus a large gain in the multiplier is not needed.<sup>7</sup>

A vibrating-reed electrometer is used to measure the output current. The vibrating-reed electrometer head and the associated electronic circuit is operated at 1000–2000 V positive with respect to ground potential.

<sup>7</sup> It has been found that the nominal gain of the multiplier cannot be maintained after cracking of the original envelope and re-mounting on our press. Rather than use activation procedures in our vacuum system with the inherent danger of damaging the surfaces of the double electrostatic analyzer, it has been decided to accept the low gain ( $10^2$ – $10^3$ ) of the multiplier. The noise limitation is the shot noise of the electron current.

The output of the vibrating-reed electrometer is brought back to ground potential by using a servo-amplifier which drives a motor to which two ten-turn potentiometers are attached on a single, insulated shaft. The first potentiometer is still at +1000 to +2000 V, whereas the second is at ground potential. This system proved to be linear and trouble-free.

A layout of the experimental arrangement is shown in Fig. 2. Two separate 300-liter/sec pumping systems communicate through a slit. The first pumping system is used to remove the molecular beam and to provide the differential pumping on the electrostatic analyzers. The second pumping system reduces the pressure in the electron multiplier chamber. Liquid air traps are used on both pumping systems. The flanges are assembled using gold gaskets. The whole system is baked at 420°C and an ultimate pressure of  $10^{-9}$  mm Hg is usually achieved.<sup>8</sup>

Details of the operation of the electrostatic analyzers have been given in part I, and the reader is referred to that discussion. Just as in part I, the basic data are exhibited on an X-Y recorder in the form of a sweep of the second electrostatic analyzer at a fixed incident electron energy. This plot gives the energy distribution of the electrons scattered at 72 deg. Figure 3 is replotted from an X-Y recorder trace for CO at an incident elec-

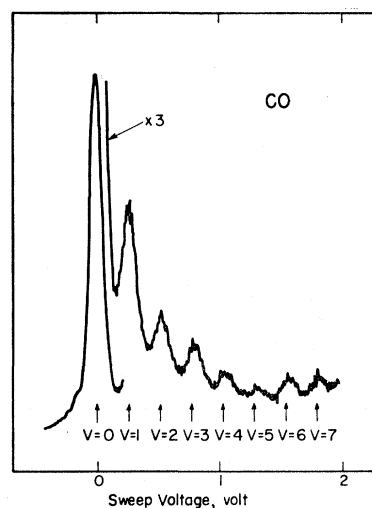


FIG. 3. Energy spectrum of scattered electrons in CO at an incident electron energy of 2.05 eV. The curve is obtained on an X-Y recorder by keeping the incident electron energy constant and sweeping the voltage on the second electrostatic analyzer. The arrows at the bottom of the figure point to the known vibrational states of CO. The first peak, marked  $v=0$  corresponds to elastically scattered electrons. Numerous curves of this type were taken in CO, H<sub>2</sub>, and N<sub>2</sub> to provide the basic data discussed in this paper.

<sup>8</sup> It has been found that baking of the system is essential for satisfactory operation of the tube and elimination of excessive contact potentials. For a proper calibration of the energy scale, it is important that any correction due to contact potentials be less than 0.1 V. This correction is established from the onset of He<sup>+</sup> N<sub>2</sub><sup>+</sup> as well as the onset of electronic excitation.

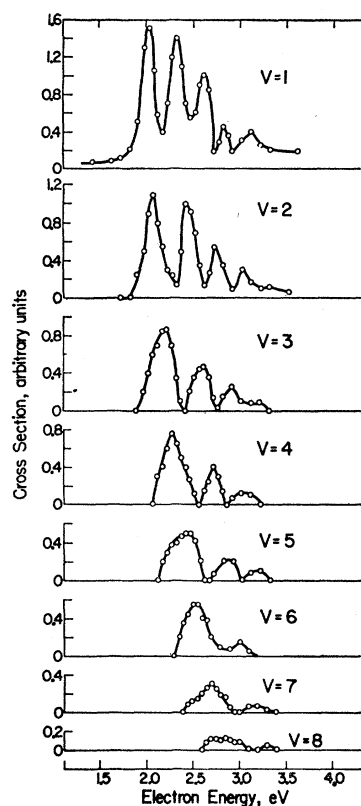


FIG. 4. Energy dependence of the vibrational cross section of nitrogen by electron impact. The curves are obtained from sets of curves similar to Fig. 3 taken at different energies of the incident electrons. When the ordinate numbers are multiplied by  $10^{-16}$  a cross-section scale (in  $\text{cm}^2$ ) is obtained such as to give a total vibrational cross section in agreement with Haas. See text for a discussion of errors in cross-section scale.

tron energy of 2.05 eV. The plot is similar to the curves shown in part I for  $\text{N}_2$  with the exception that the first vibrational state, marked  $v=1$ , is now clearly resolved.

The features described in the subsequent sections were also studied at an angle of 60 deg. This tube, a precursor of the tube shown in Fig. 1, was very similar to it except that no multiplier was used on the output. In order to incorporate an electron multiplier into this tube, the angle had to be altered to 72 deg. The half-width of the electron energy distribution is about 0.06 eV.

## II. RESULTS IN NITROGEN

Figure 4 shows the energy dependence of the vibrational cross sections obtained with the new instrument at an angle of observation of 72 deg in nitrogen. It should be noted that the cross sections for  $v=2, 3, 4, 5, 6, 7$ , and 8 have a threshold above 1.7 eV just as has been reported in part I, whereas the cross section for  $v=1$  has a long, low-energy "tail." This tail is interpreted as "direct" excitation of the first vibrational level by electron impact. An analysis of transport coefficients by Engelhardt, Phelps, and Risk,<sup>9</sup> following the methods previously discussed,<sup>10</sup> shows that this "tail" extends down to the threshold of the  $v=1$  state

<sup>9</sup> A. G. Engelhardt, A. V. Phelps and C. G. Risk, *Bull. Am. Phys. Soc.* **9**, 187, 1964.

<sup>10</sup> L. S. Frost and A. V. Phelps, *Phys. Rev.* **127**, 1621 (1962).

at 0.3 eV. The magnitude of the tail in Fig. 4 is also in approximate agreement with their analysis.

Because the elastically scattered electrons can now be separated from the primary beam, one can obtain the ratio of inelastically to elastically scattered electrons at the angle of observation. This ratio is approximately 30% at 72 deg and 15% at 60 deg at an electron energy of 2.3 eV, i.e., at the peak of the vibrational cross section. The inelastic contribution of this ratio is obtained by summing the contributions of the individual vibrational states.

It has been shown both experimentally and theoretically that the differential elastic cross section at an electron energy of 2.3 eV has a strong angular dependence, decreasing with increasing angle in the range between 60 and 72 deg,<sup>11</sup> the cross section at 72 deg being approximately 75% of that at 60 deg,<sup>12</sup> according to the experimental results. This may be the reason why the results at 60 and 72 deg are different in magnitude. The total cross section at 2.3 eV is  $2.5 \times 10^{-15} \text{ cm}^2$ .<sup>13</sup> Without knowing the details of the angular distribution of both the elastic and inelastic cross sections, it is not possible to give a reliable value for the vibrational cross section from the present experiments. Haas, from a swarm experiment, gives the total vibrational cross section at the peak to be  $3.8 \times 10^{-16} \text{ cm}^2$  which is consistent with the present result, within the severe limitations of the present experiment.<sup>14</sup> If the ordinate of Fig. 4 is multiplied by  $10^{-16}$ , an approximate cross-section scale (in  $\text{cm}^2$ ) will result, giving Haas' value for the sum of the vibrational cross sections.

The energy dependence of the elastic cross section is shown in Fig. 5. Four peaks are evident, and the position of these peaks on the energy scale fits well into the pattern established by the peaks in the vibrational cross section. This is predictable from the model proposed in part I and discussed further in the next section.

If we now add the vibrational cross sections so as to obtain the total inelastic cross section, the curve shown in Fig. 6 results. The smooth curve drawn in part I for the sum of  $v=2, 3, 4, 5, 6, 7$ , and 8 is now lost, and a secondary peak in the total inelastic cross section remains. It should be noted that the shape of the present curve for the total vibrational excitation is generally

<sup>11</sup> H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (The Clarendon Press, Oxford, England, 1952), p. 216.

<sup>12</sup> E. C. Bullard and H. S. W. Massey, *Proc. Roy. Soc. (London)* **A133**, 637 (1931).

<sup>13</sup> See Ref. 11, p. 206. The cross section given there is probably the sum of the elastic and vibrational cross sections.

<sup>14</sup> If we arbitrarily assume that both elastic and inelastic scattering is isotropic, the total vibrational cross section obtained from the present data at 60 deg would be  $3.3 \times 10^{-16} \text{ cm}^2$  agreeing with Haas' value, but data at 72 deg would give a cross section about  $5.8 \times 10^{-16} \text{ cm}^2$ , 50% higher than Haas' value. Engelhardt, Phelps, and Risk find that a cross section of  $5 \times 10^{-16} \text{ cm}^2$  is consistent with transport coefficients. It seems that the magnitude of the cross section is bracketed within a factor of two.

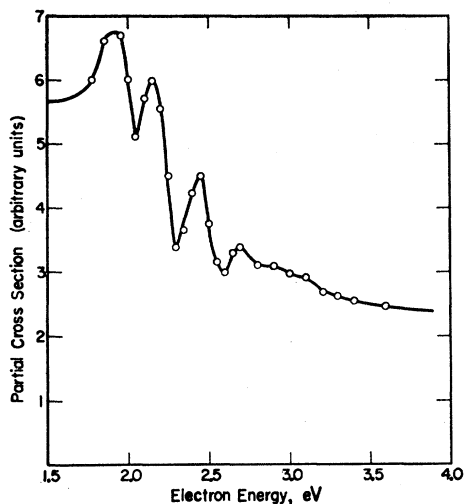


FIG. 5. Elastic scattering of electrons in N<sub>2</sub> at 72 deg versus electron energy in the energy range of the compound state.

similar to that shown in part I; a slight dip at 2.1 eV is evidenced in the curve of part I, although no significance was attached to this dip at the time; this dip is more pronounced in the present data.

### III. INTERPRETATION OF RESULTS IN NITROGEN

The interpretation discussed in part I and suggested previously<sup>15</sup> is retained for the interpretation of the results, namely, that a compound state, N<sub>2</sub><sup>-</sup>, exists around 2.3 eV. If the lifetime of the compound state is long compared to the vibration time (of the order of

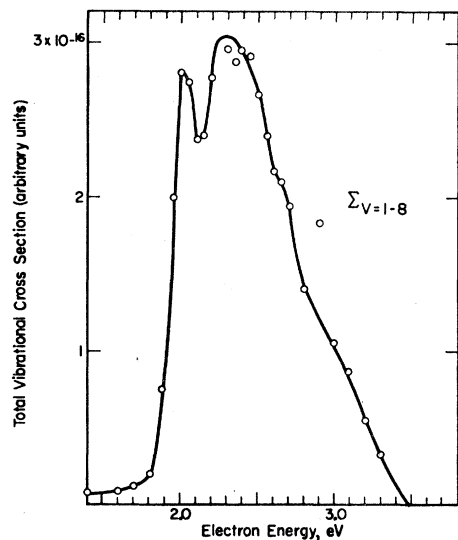


FIG. 6. Sum of the vibrational cross sections to individual states versus electron energy in N<sub>2</sub>.

10<sup>-14</sup> sec), vibrational structure would be well-developed and sharp. The incident electron excites the nitrogen molecule from its ground vibrational state  $v=0$  to a compound ( $v=0, 1, 2$ , etc.) vibrational state and the system relaxes to the various vibrational states of the ground electronic state. We can then associate the first peak for the excitation of  $v=1, 2, 3, \dots, 8$ , on Fig. 4, as proceeding via  $v=0$ . The second peak, analogously, proceeds via  $v=1$ . Using this model, all peaks with  $v=0$  should lie at the same energy. It is obvious from Fig. 4 that this is not the case. Rather, we see a shift of the  $v=0$  peak to higher energies. This fact is brought out in Fig. 7, where we plot the energy at which various peaks occur as a function of the final state of the system. The shift appears to be linear.

Herzenberg and Mandl<sup>5</sup> have recently developed a theory using the Kapur-Peierls formalism to account for the structure in the vibrational cross section. From a fit of their theory to the experimental data of part I, they arrive at the conclusion that the lifetime of the

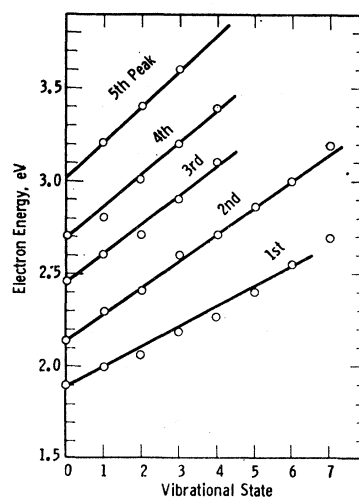


FIG. 7. Position of the cross-section peaks on the energy scale versus quantum number of the final state. On a simple long-life model of the compound state, all solid lines should be horizontal, e.g., the first peak should occur at the same energy, regardless of the final vibrational state.

compound state is comparable to the vibration time. They discuss two limiting situations, namely, (a) the "impulse limit," where the lifetime of the compound state is short compared to the vibration time, and (b) a "compound" limit, where the lifetime is long compared to the vibration time. In the latter limit, they find that the peaks all occur at the same energy, whereas the peaks occur at different energies in the impulse limit. The experimental evidence seems to point to a situation where aspects of both these limiting considerations are involved. Because the shift of the peaks of Fig. 7 is so striking, it seems that the theoretical model should offer a more satisfactory interpretation for these results.

<sup>15</sup> G. J. Schulz, Phys. Rev. **116**, 1141 (1959).

#### IV. RESULTS IN CARBON MONOXIDE

The results obtained in carbon monoxide are very similar to those obtained in nitrogen. Whereas many experiments under different experimental conditions were performed in nitrogen, only enough experiments were performed in carbon monoxide to establish the similarity in vibrational excitation of these two molecules. Figure 3 shows the energy distribution of the electrons after colliding with CO molecules, obtained by sweeping the second electrostatic analyzer while maintaining the incident electron energy at 2.05 eV. The vibrational excitation is clearly evident up to  $v=7$ . Figure 8 shows the cross section of vibrational excitation to the various states of CO. This plot is analogous to Fig. 4 for  $N_2$ . The absolute values of the cross sections were obtained assuming isotropic scattering. The total vibrational cross section, i.e., the sum of the cross sections to  $v=1, 2, 3, 4, \dots, 7$  is shown in Fig. 9. The peak of this cross section occurs at 1.75 eV and has a magnitude of 34% of the elastic, i.e.,  $8 \times 10^{-16} \text{ cm}^2$ . The position of the peak was previously found to occur at 1.7 eV, using the trapped-electron method.<sup>8</sup> It should be noted that even the magnitude of the measured cross sections is of the same order of magnitude in CO as in  $N_2$ . The confidence error in the magnitude of the absolute cross section is a factor of two.

#### V. VIBRATIONAL EXCITATION IN HYDROGEN

The problem of vibrational excitation in  $H_2$  is of great interest because of conflicting evidence. Ramien<sup>16</sup>

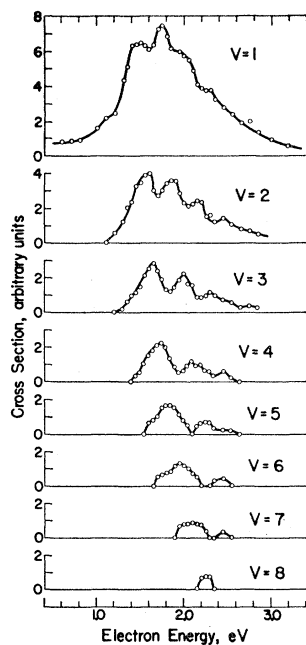


FIG. 8. Energy dependence of the vibrational cross section of CO to the first eight vibrational states. Analogous to Fig. 4.

<sup>16</sup> H. Ramien, *Z. Physik* **70**, 353 (1931). Theoretical cross sections are generally one or two orders of magnitude smaller than those quoted above. See T. Y. Wu, *Phys. Rev.* **71**, 111 (1947); and P. M. Morse, *Phys. Rev.* **90**, 15 (1953); also T. R. Carson, *Proc. Phys. Soc. (London)* **A67**, 908 (1954).

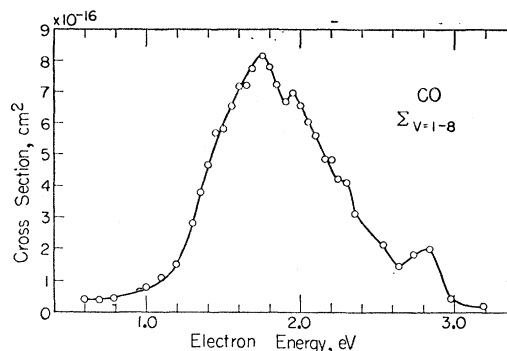


FIG. 9. Sum of the vibrational cross sections to the individual vibrational states in CO.

found a cross section for vibrational excitation at 3.5 eV to be  $4 \times 10^{-17} \text{ cm}^2$ . However, Allis and Brown<sup>17</sup> find that a vibrational energy loss of the magnitude found by Ramien is not needed for interpreting breakdown experiments in hydrogen. Others state that they need to include vibrational excitation for the interpretation of ionization coefficients.<sup>18,19</sup> The author, using the trapped electron method, was unable to find an inelastic process near the threshold of the first vibrational state in  $H_2$ .<sup>20</sup> He placed a limiting cross section of  $10^{-21} \text{ cm}^2$  for the vibrational cross section at 0.63 eV (0.1 eV above the threshold). This in itself is not in contradiction with Ramien's results since the possibility exists that the threshold for vibrational excitation occurs above 0.53 eV; this "delayed onset" is characteristic of compound states.

Recently, Frost and Phelps,<sup>10</sup> and later Engelhardt and Phelps,<sup>21</sup> performed an analysis of transport coefficients in hydrogen with the aim of extricating the rotational, vibrational, and electronic cross sections. Assuming that the shape of the theoretical cross section for rotational excitation as a function of electron energy can be extended above the vibrational threshold, they conclude that the vibrational cross section has a threshold at 0.53 eV and rises monotonically to a peak value at 4 eV. The onset at 0.53 eV is in disagreement with the results of the trapped-electron method and, thus, it seemed appropriate to re-examine the problem using the double electrostatic analyzer.

#### VI. RESULTS IN HYDROGEN

Figure 10 shows the energy spectrum of the scattered electrons at an angle of 72 deg. Only a single vibrational

<sup>17</sup> W. P. Allis and S. C. Brown, *Phys. Rev.* **87**, 419 (1952).

<sup>18</sup> A. E. D. Heylen and T. J. Lewis, *Proceedings of the Fourth International Conference on Ionization Phenomena in Gases* (North-Holland Publishing Company, Amsterdam, 1960), Vol. 1, p. 156.

<sup>19</sup> D. J. Rose, *Phys. Rev.* **104**, 273 (1956). However, the deuterium data at low  $E/p$  have been questioned by W. B. Cottingham and S. J. Buchsbaum, *Phys. Rev.* **130**, 1002 (1963).

<sup>20</sup> G. J. Schulz, *Phys. Rev.* **112**, 150 (1958).

<sup>21</sup> A. G. Engelhardt and A. V. Phelps, *Phys. Rev.* **131**, 2115 (1963).

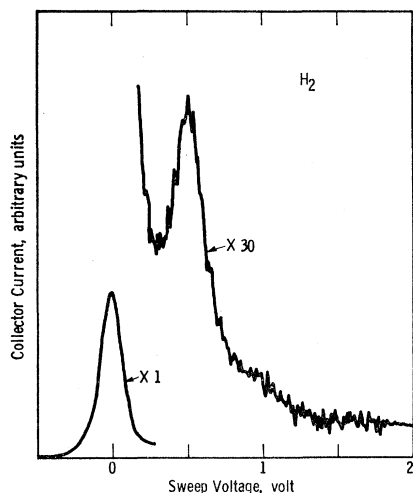


FIG. 10. Energy spectrum of scattered electrons in H<sub>2</sub>. The curve is obtained in the same manner as Fig. 3.

peak is evident in this spectrum. Figure 10 is obtained in the same manner as Fig. 3 for CO. Figure 11 shows the energy dependence of the cross section. The absolute value is obtained by assuming isotropic scattering. It is interesting to note that the assumption of isotropic scattering gives a reasonable total cross section around 3.5 eV, indicated by the agreement with Ramien's data,<sup>16</sup> shown by triangular points in Fig. 11. The curve obtained by Engelhardt and Phelps<sup>21</sup> (discussed in Sec. V) is shown dashed. Two regions of disagreement exist: The threshold of their curve occurs at 0.53 eV and their cross section is much higher above 3.0 eV.

It was thought possible originally that the disagreement in the threshold behavior results from an anomalous behavior of the rotational cross section in the vicinity of the vibrational threshold, since the theory used for predicting the rotational cross section may break down near the threshold for vibration. However, an analysis<sup>22</sup> showed that a very large, resonant-type rotational cross section would have to exist just above the vibrational threshold in order to bring the present vibrational cross section into agreement with transport coefficients. There seems to be no theoretical justification for such a resonant-type rotational cross section near the vibrational threshold at the present time. It should be noted that the threshold behavior can be analyzed from transport coefficients with very high sensitivity.

The disagreement in the magnitude of the cross section at higher energies may be due to inaccuracies in the assumed dissociation and excitation cross sections in the analysis of Engelhardt and Phelps, or due to the presence of an additional loss mechanism which has been observed in one set of experiments,<sup>20</sup> but is not understood. Frost and Phelps,<sup>10</sup> in an earlier anal-

<sup>22</sup> A. G. Engelhardt and A. V. Phelps (private communication).

ysis of transport coefficients in H<sub>2</sub> have been influenced in their vibrational cross-section determination by the data of Ramien and, therefore, their vibrational cross section fits the present data better than the results of Engelhardt and Phelps. The latter authors show that a good fit to transport coefficient cannot be obtained by a fit to Ramien's data. Neither of the above analyses have included the contribution of the cross section to the second vibrational state, which will reduce the discrepancy.

Figure 11 also shows the cross section for excitation of the second vibrational state in H<sub>2</sub> ( $v=2$ ). Its peak cross section (at 3.4 eV) is 14% of the peak cross section for  $v=1$ . It could not be traced outside the energy range indicated by the two square points.

Chen and Magee<sup>23</sup> have predicted that vibrational excitation in H<sub>2</sub> could proceed via the repulsive state of H<sub>2</sub><sup>-</sup> in the energy range 6 to 8 eV. A search in that energy range shows no vibrational excitation above the limit of the instrument, which is of the order of  $5 \times 10^{-18}$  cm<sup>2</sup>. Intuitively, a large vibrational cross section in this energy range is not expected.<sup>24</sup>

## VII. CONCLUSIONS

The data in N<sub>2</sub> and CO confirm the conclusion that vibrational excitation proceeds very efficiently via a compound state of the respective molecules located around 2.3 eV in N<sub>2</sub> and 1.7 eV in CO. Evidence for direct vibrational excitation in N<sub>2</sub> and CO has been

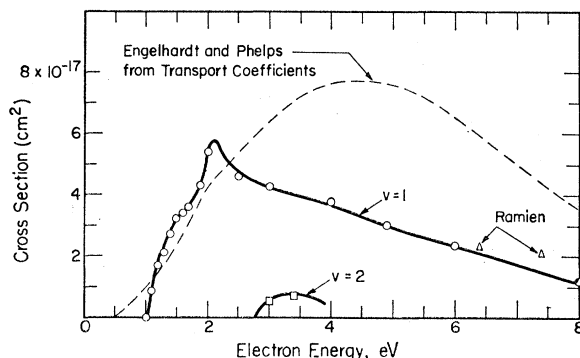


FIG. 11. Cross section for vibrational excitation of H<sub>2</sub> by electron impact. The curve marked  $v=1$  is the cross section for the first vibrational state, the curve marked  $v=2$  is for the second state. Two points obtained by Ramien are indicated. The curve of Engelhardt and Phelps is obtained from an interpretation of the transport coefficients in H<sub>2</sub>.

<sup>23</sup> J. C. Y. Chen and J. L. Magee, *J. Chem. Phys.* **36**, 1407 (1962).

<sup>24</sup> The physical reasons why a large cross section for vibrational excitation can result from a repulsive state is not understood. Normally, competition from dissociative attachment, i.e., the formation of H<sup>-</sup>+H reduces the probability of decay into vibrational states. Only when the lifetime of the repulsive state is extremely short would one expect vibrational excitation via a repulsive state to be important. The cross section for dissociative attachment has been measured [G. J. Schulz, *Phys. Rev.* **113**, 816 (1959)], and is found to be small.

found, but the cross section for the direct process is an order of magnitude lower than that for excitation via the compound state.

In hydrogen, the onset of vibrational excitation to the first vibrational state is observed above the energy level of the first vibrational state and the peak cross section is  $6 \times 10^{-17}$  cm<sup>2</sup>. These two observations, namely, the delayed onset and the large magnitude of the cross section, are indicative of the possibility that vibrational excitation in hydrogen also proceeds via a compound state located in the vicinity of 2.0 eV. Potential energy curves calculated theoretically for the H<sub>2</sub><sup>-</sup> system traverse the Franck-Condon region at much higher energies. However, Dalgarno<sup>25</sup> has raised the possibility that for small internuclear separation the theory may not approach the true potential energy curve for H<sub>2</sub><sup>-</sup>. Further theoretical work will be needed before this question can be resolved.

The results in H<sub>2</sub> are in agreement with the results of the trapped electron method near threshold and the results of Ramien at 3.5 eV, but disagree with the results of Englehardt and Phelps. The latter disagreement should not overshadow the fact that a large cross section for vibrational excitation in hydrogen is now well established.

More evidence is accumulating pointing to the fact that compound states play a dominant role in collisions between electrons and atoms or molecules. Examples are the vibrational excitation discussed in this

paper, the resonance found in the elastic scattering of helium and neon,<sup>26</sup> the two-electron excitation in helium,<sup>27</sup> the theoretical prediction of a resonance in atomic hydrogen,<sup>28</sup> and negative ion formation,<sup>29</sup> the theoretical considerations of Baranger and Gerjuoy,<sup>30</sup> and the autoionizing states, whose lifetime has been recently determined.<sup>31</sup>

#### ACKNOWLEDGMENTS

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<sup>26</sup> G. J. Schulz, *Phys. Rev. Letters* **10**, 104 (1963). The results in neon have been presented at the Third International Conference on the Physics of Electronic and Atomic Collisions, London, 1963 (unpublished). See also R. J. Fleming and G. S. Higginson, *Proc. Phys. Soc. (London)* **81**, 974 (1963); and J. A. Simpson and U. Fano, *Phys. Rev. Letters* **11**, 158 (1963).

<sup>27</sup> S. M. Silverman and E. N. Lassette, *J. Chem. Phys.* **40**, 1265 (1964); and U. Fano, *Phys. Rev.* **124**, 1866 (1961).

<sup>28</sup> P. G. Burke and H. M. Schey, *Phys. Rev.* **126**, 147 (1962); also, A. Temkin and R. Pohle, *Phys. Rev. Letters* **10**, 22 (1963).

<sup>29</sup> It has been shown that negative ion formation (O<sup>-</sup>) from N<sub>2</sub>O proceeds via a compound state. See G. J. Schulz, *J. Chem. Phys.* **34**, 1778 (1961).

<sup>30</sup> E. Baranger and E. Gerjuoy, *Proc. Phys. Soc. (London)* **A72**, 326 (1958).

<sup>31</sup> P. Feldman and R. Novick, *Phys. Rev. Letters* **11**, 278 (1963).

<sup>25</sup> A. Dalgarno (private communication).