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Rotational and Vibrational Excitation of H₂ by Electron Impact at 4.5 eV: Angular Distributions*

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The differential cross sections for rotational, vibrational, and rotational-vibrational excitation by electron impact at 4.5 eV in H₂ have been measured with a resolution of 18–22 meV. The cross-section ratio of pure vibrational excitation ($\Delta j = 0$) to rotational-vibrational ($j = 1 \rightarrow 3$) excitation for $v = 1, 2,$ and 3 shows the expected p -wave character. However, at a given angle of observation, this ratio decreases as the vibrational quantum number increases. This effect has not been predicted by theory.

Electron impact on the hydrogen molecule at low energies¹ is strongly influenced by the existence of a shape resonance, $^2\Sigma_u^+$, which is several eV wide and is centered near 2–3 eV. Decay of this resonance may lead to pure rotational excitation ($\Delta j = +2$), to superelastic rotational de-excitation ($\Delta j = -2$), to pure vibrational excitation ($v = 0 \rightarrow 1, 2, 3, 4; \Delta j = 0$), and to vibrational excitation accompanied by rotation ($v = 0 \rightarrow 1, 2, 3; \Delta j = 1 \rightarrow 3$). Also, decay into H⁻ + H, i.e., dissociative attachment, has been observed in the tail of the shape resonance above 3.75 eV.

Much of our knowledge regarding the existence of this low-lying resonance—which serves as a prototype for many other molecules—comes from measurements of the angular distribution of the scattered electrons. Particular attention has been given to the measurement of the angular distribution of electrons having excited the $v = 1$ vibrational state, accompanied by a change of the rotational quantum number $\Delta j = 2$ or $\Delta j = 0$. Such data have provided the testing ground for various theoretical approaches.^{2,3}

We have recently improved our electron spectrometer sufficiently in both resolution and sensitivity so that we are now able to measure an-

gular distributions not only for $v = 1$, but also for $v = 2$ and $v = 3$, and still resolve the rotational components accompanying these vibrational transitions. The data reported here should serve as a much more refined test of theories than have been available previously.

The apparatus used for the present study consists of a rotatable hemispherical electrostatic monochromator and a similar analyzer, with a molecular beam crossing the path of the electrons in the collision region. This apparatus has been described by Boness and Schulz.⁴ However, the energy resolution and the signal intensity for elastically scattered electrons have been significantly improved as a result of the optimization of electron-lens operation, electrostatic shielding in the collision region, and the use of a larger length-to-diameter ratio of the molecular-beam nozzle. For the 18–22-meV resolution (full width at half-maximum for the energy-loss peak) adopted in this study, typical elastic counting rates are 4×10^3 counts/sec at a hydrogen background pressure of 2×10^{-5} Torr.

Energy-loss spectra with incident electron energy fixed at 4.5 eV are obtained for scattering angles ranging from 20 to 100°, for energy losses

up to $v=0 \rightarrow 3$ and the associated rotational transitions. Because the inelastic cross sections decrease rapidly (about a factor of 10) with increasing vibrational quantum number, a more economical averaging approach is adopted to improve the overall signal-to-noise ratio of the small peaks for $v=2$ and $v=3$. This involves the use of an on-line PDP-11 computer as a multi-data-block signal averager. Each data block is assigned to cover the required energy range of all rotational transitions associated with a particular vibrational quantum jump. The dwell time for each datum point in a given block is adjusted according to the maximum peak signal intensity to yield roughly uniform signal-to-noise ratios for all energy-loss loss peaks.

Absolute differential cross sections for rotational, vibrational, and rotational-vibrational excitations in H_2 are obtained in two steps as previously described.⁵ First, we measure the ratio of the peak height of inelastic to the elastic peaks in the energy-loss spectrum and we derive the ratio of cross sections by using the appropriate initial populations.⁶ Second, the elastic differential cross section in H_2 is obtained by comparing the elastically scattered current in H_2 with that in He at the same gas density and by normalizing to the known differential cross sections of He as calculated by LaBahn and Callaway.⁷ Thus the absolute values of the differential cross sections reported in this paper are based on the calculated

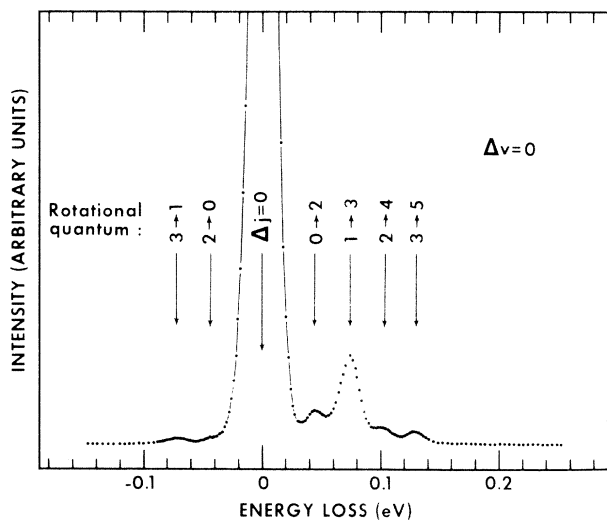


FIG. 1. Energy-loss spectrum for rotational excitation ($\Delta j=+2$) and superelastic ($\Delta j=-2$) transitions in H_2 . The incident energy is 4.5 eV and the scattering angle is 60° .

cross sections of LaBahn and Callaway in helium.

Figure 1 shows an energy-loss spectrum for pure rotational excitation and deexcitation. The energy levels for rotational transitions from $j=0, 1, 2,$ and 3 with $\Delta j=+2$ and for superelastic transitions from $j=2$ and 3 with $\Delta j=-2$ are indicated with arrows in the figure. The relative peak heights for all the inelastic transitions are consistent with the cross-section ratios predicted by Gerjuoy and Stein⁸ and with the assumption that the gas is in equilibrium at $298^\circ K$. A large-scale energy-loss spectrum obtained with four data blocks ($v=0, 1, 2, 3$) is shown in Fig. 2. The decrease in the spacing between adjacent rotational peaks for increased vibrational quantum is due to the fact that an anharmonically vibrating hydrogen molecule has a larger moment of inertia.

Figure 3 shows the angular dependence for differential cross sections, in absolute units. For each vibrational transition ($v=0 \rightarrow 1; v=0 \rightarrow 2; v=0 \rightarrow 3$) we show two curves: one for no change in rotational quantum number ($\Delta j=0$) and the other for $\Delta j=1 \rightarrow 3$. For the "elastic" region ($v=0 \rightarrow 0$) we show the "pure rotational" transition, $j=1 \rightarrow 3$. All cross sections which involve a change in rotational quantum numbers are nearly isotropic, although we consider the slight downward slope on some of the curves real. All vibrational cross sections with $\Delta j=0$ exhibit approximately a p -wave behavior. The magnitude of all inelastic cross sections associated with a given vi-

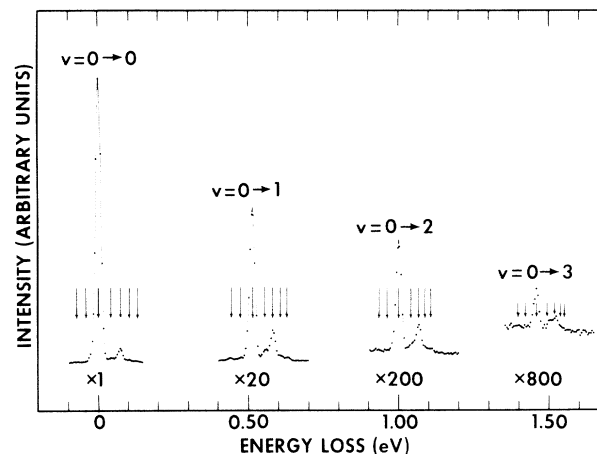


FIG. 2. Energy-loss spectrum of H_2 at an incident energy of 4.5 eV and scattering angle of 40° showing vibrational excitation up to $v=3$. The arrows associated with the data block of each vibrational quantum have the same meaning as in Fig. 1. The vertical gain (relative dwell time) for each data block is shown.

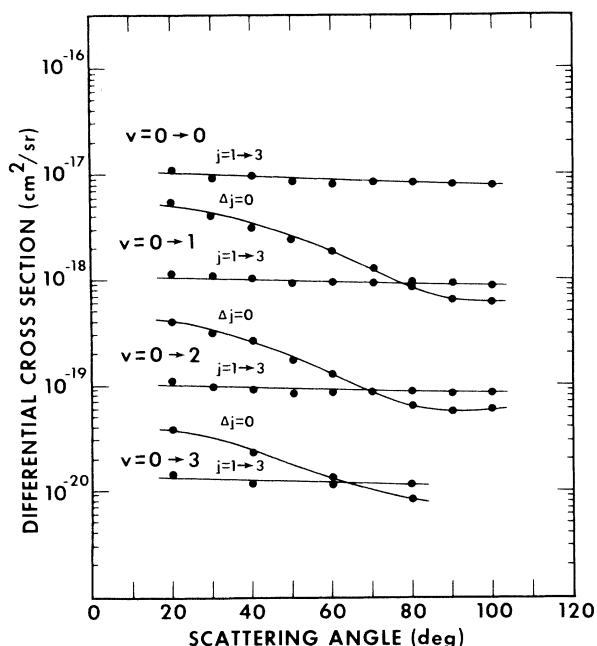


FIG. 3. Angular dependence of the absolute differential cross sections for rotational ($v=0 \rightarrow 0, j=1 \rightarrow 3$), vibrational ($v=0 \rightarrow 1, 2, 3, \Delta j=0$), and rotational-vibrational ($v=0 \rightarrow 1, 2, 3, j=1 \rightarrow 3$) excitations.

brational quantum decreases by a factor of 10 as v increases by unity.

The experimental errors in the *absolute* magnitude for all inelastic cross sections except for $v=3$ are estimated to be about 10%. A 15% experimental error is assigned to the absolute magnitude of the cross section for $v=3$ to take into account the statistics of the much weaker signal. This error does not apply to *relative* magnitudes or ratios, for which we estimate the error to be about 5% for $v=1$ and $v=2$ and less than 10% for $v=3$. The absolute results on magnitudes for the differential inelastic cross sections for $v=0$ and $v=1$ agree with those reported by Linder and Schmidt⁹ within 5–10%, which we consider excellent agreement in view of the fact that the methods of calibration are completely different in the two experiments.

Figure 4 shows the angular dependence of the ratio of pure vibrational cross section to rotational-vibrational cross section, with the vibrational quantum number, $v=1, 2, 3$, as a parameter; i.e., we plot $R = \sigma(\Delta j=1)/\sigma(j=1 \rightarrow 3)$ for $v=0 \rightarrow 1$, $v=0 \rightarrow 2$, and $v=0 \rightarrow 3$. Shown for comparison in Fig. 4 are the experimental results of Linder and Schmidt,⁹ who studied only $v=0 \rightarrow 1$ and thus could not observe the decrease in R as the vibrational

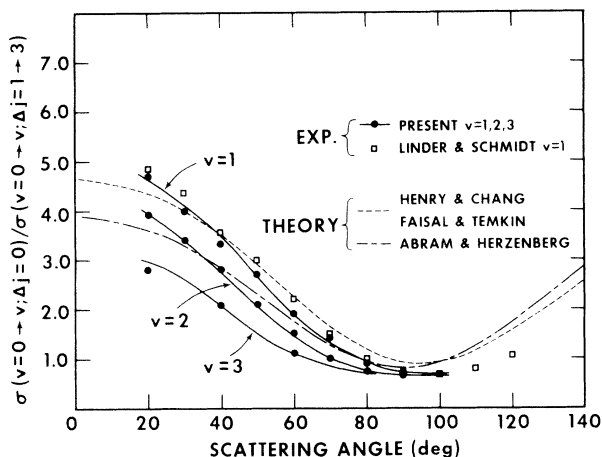


FIG. 4. Angular dependence of the cross-section ratio $\sigma(\Delta j=0)/\sigma(v=0 \rightarrow v; \Delta j=1 \rightarrow 3)$ for $v=1, 2$, and 3 .

quantum number increases.

There are four recent theoretical papers on vibrational excitation in the 4.5-eV region with which we could compare the present experimental results, especially the ratio plotted in Fig. 4. We expect that the theory of Henry and Chang¹⁰ supersedes that of Henry,¹¹ leaving three theories. The results of Henry and Chang¹⁰ and those of Faisal and Temkin¹² are very similar so that they can be assumed to be one (HCFT). Despite the different verbiage used in the two papers, it appears that the approximations which were made by Henry and Chang¹⁰ in the "frame-transformation theory" reduced this theory to the "adiabatic-nuclei theory," also called the "impulse approximation." Thus we have only two different results left, that of Abram and Herzenberg¹³ (AH) and that of HCFT discussed above. Both of these calculations assume that the *interaction time of the projectile with the molecule is short compared to a rotational period*. The theory of AH neglects direct excitation and assumes that only scattering via the $^2\Sigma_u^+$ compound state contributes. No such assumptions have been made by HCFT.

Both AH and HCFT have calculated the ratio $R = \sigma(\Delta j=0)/\sigma(j=1 \rightarrow 3)$, and the comparison between these two calculations and the experiments is made in Fig. 4. It appears that the calculation of HCFT predicts the shape of the ratio curve for $v=1$ in a fairly satisfactory way but it has not been applied to the higher vibrational states. The theory of AH, by neglecting the direct component of scattering and only using the resonance component, is probably more applicable for $v=2$ and $v=3$ since the excitation to these states is entirely

due to the ${}^2\Sigma_u^+$ resonance. The calculation of AH agrees fairly well with the experimental curve for $v=2$. However, in the resonance theory of AH, the scattering amplitude consists of a product of the vibrational and angular excitations; thus the ratio R should be *independent of vibrational transition* provided that the p -wave component alone is involved in the reaction. Herzenberg¹⁴ points out that this would not be the case if higher partial waves (e.g., f wave) should mix with the p wave in such a manner that their relative amplitudes depended on the internuclear separation.

One may ask whether the assumption used in all calculations, namely that the interaction time of the projectile with the molecule is short compared to a rotational period, is appropriate. Herzberg¹⁵ points out that in order for this approximation to be valid, we must have $\Delta E_r/\Gamma \ll 1$. Here, ΔE_r is the rotational spacing and Γ is the width of the resonance. In our case, the ratio $\Delta E_r/\Gamma$, which represents the ratio of the electronic time delay to the rotational period, is of the order of 0.02 so that the use of the "adiabatic-nuclei theory" is amply justified.

In conclusion, we have extended the experimental evidence for rotational-vibrational excitation of H_2 to higher vibrational states and we find that the $j=1 \rightarrow 3$ transition for $v=1, 2,$ and 3 shows an isotropic behavior, as predicted by the theory. However, we find that the ratio $R = \sigma(\Delta j=0)/\sigma(j=1 \rightarrow 3)$ is dependent on vibrational excitation. This result has not been predicted by any theory so far and it is rather surprising.

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