

## ION-IMPACT EXCITATION OF PURE VIBRATIONAL TRANSITIONS IN DIATOMIC MOLECULES\*

John H. Moore, Jr.,<sup>†</sup> and John P. Doering<sup>‡</sup>

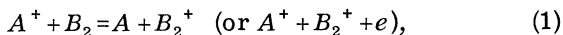
Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

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An ion-impact spectrometer has been constructed to measure the energy loss of ions inelastically scattered without charge exchange from molecular targets. Pure vibrational transitions excited by  $H^+$  and  $H_2^+$  projectiles of energies from 100 to 600 eV have been observed in  $H_2$ ,  $D_2$ , and  $N_2$ . The angular distribution of scattered ions and the energy dependence for these processes have been investigated. The excitation cross sections for pure vibrational transitions are unusually large.

In this paper, we wish to report the observation of pure vibrational transitions in  $H_2$ ,  $D_2$ , and  $N_2$  produced by low-energy (100- to 600-eV) proton impact. Although pure vibrational excitation of molecules by electrons has been observed for many systems,<sup>1-3</sup> there appears to be no previous experimental evidence for such transitions in the case of ion impact. We have found that the excitation cross sections for ion-impact induced vibrational transitions are remarkably large; they are, in fact, several orders of magnitude larger than for the electron impact case.

An unreactive, inelastic collision between an ion and a molecule may proceed by one of two channels:



where  $B_2^*$  denotes a target molecule which has been left in an excited state. The first channel (1) includes charge-transfer processes and ionization. Either or both of the products of (1) may also, of course, be excited. Recent optical studies of channel (1) using nitrogen targets<sup>4-6</sup> have shown that for low-energy projectile ions, electronic excitation of the products is accompanied by extensive rotational and vibrational excitation. In order to study non-charge-transfer processes, denoted by channel (2), we have constructed an ion spectrometer to measure the kinetic energy loss of ions which are inelastically scattered in collisions with molecules. The apparatus consists of two major parts—a monochromator to velocity analyze the previously mass-analyzed primary ion beam, and an articulated analyzer to velocity analyze ions which are scattered at various angles from the target gas. In early survey spectra of protons of a few hundred eV energy scattered from  $H_2$  and  $N_2$ , we observed that one of the most prominent features of the energy-loss spectrum corresponded to ions which had been scattered with energy losses of only a few

tenths of an electron volt. By the use of various target gases, we have been able to assign these inelastically scattered ions to collisions which result in pure vibrational excitation of the target molecule.

The source of mass-analyzed ions for the ion spectrometer has been described previously.<sup>4</sup> It is a multistage device in which a duoplasmatron ion source is floated above ground at a potential equal to the desired final ion energy. The 60° magnetic mass analyzer following the source is maintained at -10 kV so that ions are extracted from the source and transported at high energies. In the present experiment, the beam is decelerated to a few eV and velocity analyzed to produce monochromatic ions. The beam is then reaccelerated and focused into the collision chamber, which contains the target gas. Ions scattered through a given angle enter a second energy analyzer where the kinetic energy loss from the collision is determined.

120° spherical electrostatic deflectors serve as energy analyzers for both the primary beam and the scattered ions. The ions pass through the deflectors at a fixed, low energy (6-12 eV). A decelerator lens on the input and an accelerator lens on the output of each deflector produce virtual images of the entrance and exit apertures at the respective focal planes of the spherical deflectors. Typically, with 0.020-in.-diam apertures, the energy resolution of these analyzers is 100-200 meV full width at half-maximum.

The energy-loss spectrum is scanned by adding back the energy lost in collision. In this way, the analysis energy of the ions as they pass through the electrostatic deflectors remains constant so that the resolution does not change as the spectrum is scanned. The adder lens system has been described elsewhere.<sup>7</sup> This lens system acts as an achromatic electron optical lens and allows the energy lost in collision to be added back without changing the transmission of the analyzer.

Ions which pass through the analyzer are accelerated to about 3 keV and detected with an electron multiplier. In these experiments the output current from the multiplier was measured by an electrometer which in turn drove the  $Y$  axis of an  $X$ - $Y$  recorder. The spectrum was scanned by a linear voltage-ramp generator which drove the analyzer scan as well as the  $X$  axis of the recorder.

A problem encountered in a high energy-resolution measurement of heavy-particle scattering is that appreciable kinetic energy may be transferred elastically from projectile to target. For example, in laboratory coordinates,  $2^\circ$  elastic scattering of a 200-eV proton by  $H_2$  results in the transfer of about 120 meV of kinetic energy. As a result, the energy resolution of the ion spectrometer is coupled to its angular resolution. That is, finite angular resolution introduces some uncertainty into the energy measurement because the amount of energy transferred elastically to the target is uncertain. Thus, finite angular resolution will produce some smearing of the energy-loss spectrum. This effect is not observed when the analyzer scans the unscattered primary beam from the monochromator. In our apparatus, the angular resolution is about 0.035 rad ( $1.75^\circ$ ) which places an upper limit of about 150 meV on the effective resolution available.

The static target gas is contained in a collision chamber which is 3.8 cm in diam. Ions enter and leave the collision chamber through 0.020-in. apertures. The target gas pressure outside the collision chamber is effectively zero. Because the angular resolution of the scattered ion analyzer is of the same order of magnitude as the typical scattering angles used for these experiments, the scattering volume is assumed to extend from the primary beam inlet to the opposite wall of the collision chamber. That is, the primary beam path length has been taken to be 3.8 cm at all scattering angles.

Figure 1(a) shows the energy-loss spectrum of 200-eV protons scattered in the forward direction ( $\theta = 0^\circ$ ) from molecular hydrogen. The peak at 0-eV energy loss corresponds to unscattered ions. The peaks at about 0.5, 1.0, 1.5, and 2.0 eV have been assigned to transitions to the  $v' = 1, 2, 3,$  and 4 vibrational levels of the target  $H_2$  molecule. This assignment is confirmed in Fig. 1(b) which is the energy-loss spectrum of 200-eV  $H^+$  scattered from  $D_2$ . The four inelastic peaks are shifted to approximately  $1/\sqrt{2}$  the en-

ergy of the  $H_2$  peaks.

The maxima of the peaks in the energy loss spectrum are systematically displaced to slightly higher energies than are given by the positions of the vibrational energy levels. The Boltzmann rotational energy distribution in the ground state of  $H_2$  peaks below  $J=1$  and would not account for the displacement of the peak of the envelope of each vibrational level. However, we have shown that low-energy ion impact produces extensive excitation to high rotational levels,<sup>4,5</sup> and that this effect may account, in part, for the position of the observed peak in the rotational envelope. Elastic transfer of kinetic energy from projectile to target probably also accounts for some of the additional energy loss in these collisions.

Figure 2 gives the angular profiles of the  $v' = 1$  and  $v' = 2$  peaks compared to the profile of the unscattered beam. The three sets of data have been normalized to the same maximum intensity. The angular profile of the two inelastic peaks is

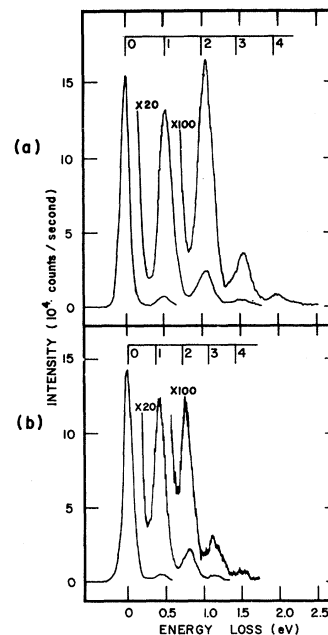


FIG. 1. (a) Energy-loss spectrum of 200-eV protons scattered from molecular hydrogen. The scattering angle was  $0^\circ$  and the target gas pressure was 3.5 mTorr. The positions of the  $v' = 1, 2, 3,$  and 4 vibrational levels of the ground state of  $H_2$  are indicated relative to the  $v' = 0$  level at 0-eV energy loss. (b) Energy-loss spectrum of 200-eV protons scattered from deuterium. The scattering angle was  $0^\circ$  and the target gas pressure was 3 mTorr. The positions of the  $v' = 1, 2, 3,$  and 4 vibrational levels of the ground state of  $D_2$  are indicated relative to the  $v' = 0$  level at 0-eV energy loss.

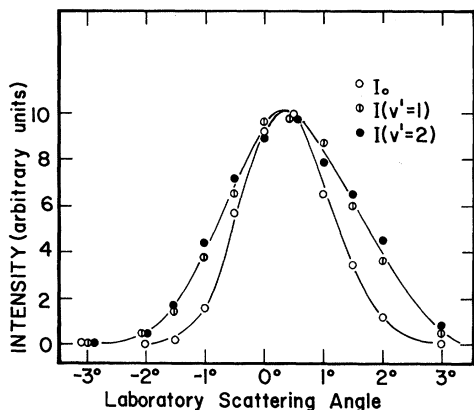


FIG. 2. Intensity as a function of angle of the (0-1) and (0-2) peaks in the spectrum of  $H_2$  excited by 200-eV proton impact. The angular profile of the unscattered beam is also shown. The three sets of data have been normalized to the same maximum intensity. The target gas pressure was 3.5 mTorr.

obviously broader than the primary beam profile. Within experimental error, the shapes of the differential cross-section curves for the  $v'=1$  and  $v'=2$  peaks are identical; the collision parameters for the (0-1) and (0-2) transitions are therefore indistinguishable. The possibility of a contribution to the differential scattering cross sections from elastically scattered ions must be considered. The  $v'=1$  peak of  $H_2$  is at 0.5 eV. A simple calculation shows that elastically scattered protons which have lost 0.5 eV are scattered through about  $4^\circ$ . Since we do not detect any intensity beyond about  $3^\circ$ , elastic scattering cannot contribute to the  $v'=1$  inelastic differential cross section for the case of  $H^+$  on  $H_2$ .

The available range of proton energies in these experiments was 100-600 eV. The energy dependence of the proton-excited spectra was investigated throughout this range. At constant pressure, the intensity of the (0-1) transition,  $I(v'=1)$ , relative to that of the 0-eV peak (unscattered ions)  $I_0$  remained constant to within 20%. The intensity ratio compares favorably with the 10-eV electron-excited spectrum of Trajmar *et al.*<sup>1,8</sup>

The total scattering cross section was determined by measuring the attenuation of the unscattered beam as a function of pressure with the analyzer at  $0^\circ$  scattering angle. The beam attenuation cross section was found to increase from  $5 \times 10^{-16}$  to  $9 \times 10^{-16}$   $cm^2$  as the projectile energy was lowered from 600 to 100 eV. The total scattering cross section in this energy range has been measured previously by Cramer<sup>9</sup> with about one-half the angular resolution ( $0.073$

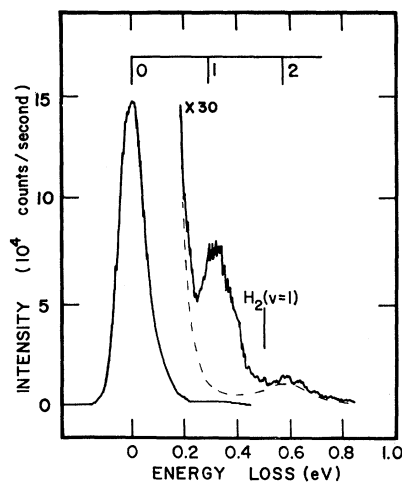


FIG. 3. Energy-loss spectrum of 150-eV protons on  $N_2$ . The scattering angle was  $0^\circ$  and the target gas pressure was 5 mTorr. The dashed line is the apparent energy profile of the primary beam with no nitrogen in the collision chamber. The (0-1) peak of  $H_2$  is present because  $H_2$  from the ion source is an unavoidable background gas.

rad) used for this experiment. Cramer's experiment did not include energy analysis, so there was no discrimination against inelastic forward scattering. The cross section from our apparatus is five times larger than the total scattering cross section (the sum of "elastic" and "inelastic" cross sections) reported by Cramer. This result is reasonable since we include smaller angle elastic scattering as well as inelastic forward scattering in our definition of the total scattering cross section.

With the data discussed above, the total cross section for ion-impact-excited vibrational transitions in  $H_2$  may be determined. The intensity of the 0-eV peak in the energy-loss spectrum may be corrected to give the intensity of the primary beam by making use of the measured attenuation cross section. The intensity of any inelastic peak at  $0^\circ$  may be corrected for the difference between the angular profile of the primary beam and the intensity profile of the inelastically scattered ions by making use of the data from Fig. 2. Thus the cross section for the (0-1) transition in  $H_2$  has been estimated to be  $(1.7 \pm 0.5) \times 10^{-16}$   $cm^2$  for proton-impact excitation in the energy range 100-600 eV.

The ion-impact spectrum of protons on molecular nitrogen was also measured. The  $0^\circ$  energy-loss spectrum of 150-eV  $H^+$  on  $N_2$  is presented in Fig. 3. This spectrum was taken with the best energy resolution obtained with our instrument.

The (0-1) peak is well resolved. Unfortunately, the (0-2) transition is obscured by the (0-1) transition of  $H_2$  since  $H_2$  from the ion source is present as a background gas throughout the vacuum system at a pressure of about  $1 \times 10^{-5}$  Torr.

The angular distribution of the inelastically scattered ions was not measured for the  $N_2$  case. We can place a lower limit on the cross section for vibrational excitation if we assume that the angular distribution, in laboratory coordinates, of inelastically scattered ions is broader for  $N_2$  targets than for  $H_2$ . This broadening is expected because of the greater mass disparity between projectile and target in the case of  $H^+$  on  $N_2$  as compared to  $H^+$  on  $H_2$ . From our spectrum we can estimate the cross section for proton-impact excitation of the (0-1) transition in  $N_2$  to be at least  $3.6 \times 10^{-17}$  cm<sup>2</sup> at 150 eV.

Pure vibrational transitions to the  $v'=1, 2$ , and 3 levels of  $H_2$  were observed in the energy-loss spectrum of  $H_2^+$  scattered from  $H_2$ . In these spectra, the vibrational peaks were not completely resolved because of reduced resolution as a consequence of the greater elastic transfer of kinetic energy which occurs in the collisions of the heavier  $H_2^+$ . Throughout the energy range 100-600 eV, there was no observable energy dependence of the relative intensity of the peaks in the spectrum. The measured cross section for exciting the  $v'=1$  level of  $H_2$  by  $H_2^+$  impact is  $(4.8 \pm 1.3) \times 10^{-17}$  cm<sup>2</sup>.

The large cross section for pure vibrational excitation by ion impact is surprising when compared with the corresponding electron-excitation case. Excitation of a pure vibrational transition in the ground state of a homonuclear diatomic molecule is electric-dipole forbidden. Ground-state vibrational excitations have, however, been observed for electron-impact excitation. Schulz<sup>10</sup> has observed these transitions in  $H_2$  and  $N_2$  at low electron energies (2-3 eV). His measured cross sections are quite large—about  $10^{-16}$  cm<sup>2</sup>. At these low energies, the excitation is thought to be a resonance process which proceeds by way of negative ion formation. At energies too high for the resonance process to be important, these same transitions have been observed, although with much smaller cross sections. Trajmar, Rice, and Kupperman<sup>8</sup> have reported the differential cross section for excitation of the (0-1) transition in  $H_2$  by 81.6-eV electrons. Their data indicate a total cross section of about  $1.1 \times 10^{-18}$

cm<sup>2</sup>. Skerbele, Dillon, and Lassette<sup>2</sup> have estimated the total cross section for the excitation of the (0-1) transition in  $N_2$  by 45-eV electrons to be about  $4 \times 10^{-19}$  cm<sup>2</sup>. The proton energies used in our experiments are too large for the excitation to be considered a resonance process, so it is remarkable that they occur so strongly.

Because of the small probability of a pure vibrational transition in a homonuclear diatomic molecule, the transitions observed in this work must take place as a result of the strongly perturbing effect of the projectile ion. That is, the transition must take place while the target molecule is distorted by the field of the nearby projectile ion. As the perturbing ion departs, the excited molecule is apparently very effectively trapped in the upper vibrational state.

Since the cross section for proton-impact excitation of pure vibrational transitions is of the same order of magnitude as other inelastic processes (such as charge exchange),<sup>11,12</sup> vibrational excitation must be an important factor in the stopping of protons by gases. Such excitation may also cause vibrational heating of the target gas. These effects may be important, for example, in the upper atmosphere at times when large fluxes of low-energy protons are present.

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†Present address: Department of Chemistry, University of Maryland, College Park, Md.

‡Alfred P. Sloan Fellow.

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