Near-Threshold Vibrational Excitation of H_2 by Electron Impact: Resolution of Discrepancies between Experiment and Theory

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New measurements and calculations of near-threshold (0.5–5.0 eV) e-H_2 vibrational-excitation cross sections challenge previous determinations based on transport analysis. Elastic and $v_0=0\rightarrow v=1$ cross sections measured in a crossed electron-molecular-beam apparatus agree well with values calculated using a vibrational close-coupling theory with a separable representation of exchange, particularly at energies below 2.0 eV, but are incompatible with cross sections derived via analysis of electron-swarm transport data.

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Of the many experimental techniques for determining very-low-energy absolute electron scattering cross sections, the two most commonly used are the single-collision or crossed-beam method, which directly measures the cross section, and an indirect method based on a solution of the Boltzmann equation for a swarm of electrons drifting and diffusing through a gas under the influence of an applied external field. At energies below a few tenths of an eV, the latter method is the only viable way to determine momentum transfer and inelastic cross sections.

An important confirmation of collision theory and atomic structure came in 1979 when Nesbet calculated *ab initio* low-energy e-He scattering cross sections[1] that agreed with swarm-derived values[2] to 1%. That same year researchers at the University of Oklahoma (OU) and the Australian National University (ANU) undertook an analogous study for the simplest electron-molecule system, e-H_2; at that time low-energy (i.e., electronically elastic) cross sections for this system were plagued by uncertainties and inconsistencies.[3] For example, early swarm-derived vibrational-excitation cross sections[4] differed from those measured in early crossed-beam experiments[5,6] by as much as 60%.

Unexpectedly, this collaboration yielded another significant discrepancy. Although swarm-derived cross sections for elastic scattering and rotational excitation agreed with the new calculated results, those for the $v_0=0\rightarrow v=1$ cross section $\sigma_{0\rightarrow 1}^{(v)}$ did not: From threshold (at 0.52 eV) to 1.5 eV, the derived and theoretical values for this cross section disagreed by as much as 60%—many times the most pessimistic error estimates for either determination.[7,8]

The present collaboration attempts to resolve the discrepancy in the value of $\sigma_{0\rightarrow 1}^{(v)}$ by combining measurements (at the ANU) using a new crossed-beam apparatus developed for low-energy collisions and calculations [at OU and the Joint Institute for Laboratory Astrophysics (JILA)] from a new theoretical formulation that incorporates a rigorous treatment of the nonlocal exchange interaction, which in previous research we approximated by a model potential.

Early beam experiments[5,6] sought to study the effect of resonances on vibrational and electronic excitation, not to measure absolute cross sections. Moreover, the current situation requires more precise specification of the measured cross sections than has been hitherto available. The present crossed electron-molecular-beam apparatus, which is described in detail elsewhere,[9] was designed to yield absolute cross sections, with careful attention to the identification and quantification of errors.

We have measured absolute differential e-H_2 cross sections (DCS) at seven energies between 1.0 and 5.0 eV over an angular range from 5° to 130°. The overall energy resolution of these measurements, 90 meV, enables us to resolve H_2 vibrational (but not rotational) states. This renders our results directly comparable to those from transport analysis, which can determine integrated vibrational but not rovibrational cross sections. We calibrated the energy of the incident beam against the energy of the 2^2S resonance of He, 19.367 eV.[10] To assign absolute values to the measured relative elastic angular distributions we used the relative flow technique[11] and calculated values of the elastic e-He cross sections[1] as a reference standard. We then obtained absolute vibrational-excitation cross sections by measuring ratios of elastic to vibrational excitation at several scattering angles at each energy.[9] We estimate the uncertainty in the

resulting differential cross sections to be 8% for elastic scattering and 14% for vibrational excitation. To obtain $\sigma_{0\rightarrow 1}^{(v)}$ we extrapolate the vibrational DCS to 0° and 180°; we estimate the total uncertainty in this integrated vibrational-excitation cross section to be ± 20%.

In previous theoretical studies of vibrational excitation, we approximated the nonlocal exchange effects by a local, energy-dependent model potential optimized for inelastic collisions.[12] Because of the great importance of exchange for vibrational excitation and the severity of the disagreement between calculated and swarm-derived cross sections, we have eliminated this approximation and here treat the exchange operator as properly nonlocal within a separable representation. This change altered $\sigma_{0\rightarrow 1}^{(v)}$ by 5% to 10% over the energy range considered in this paper.

We expand the exchange kernel in a basis of symmetry-adapted $\mathcal{L}^2$ functions (the bound and virtual molecular orbitals of the ground state of H_2) constructed from a set of Cartesian Gaussian functions. We have found vibrational excitation to be acutely sensitive to the representation of the nonlocal exchange potential and have developed a procedure for systematically converging this representation; a report of this work will appear elsewhere.[13] Details concerning our treatment of the additional terms in the interaction potential—the electrostatic and correlation-polarization potentials—have recently been published.[14]

The wave function for an electron engaged in vibrational excitation is acutely sensitive to the vibrational dynamics of the target, so it is essential to accurately allow for the effect of nuclear motion on the scattering function.[15] We do so via the body-frame vibrational close-coupling (BFVCC) theory, which incorporates vibrational effects exactly and rotational effects adiabatically.[3,16] We have demonstrated previously that for e-H_2 scattering this treatment of the vibrational and rotational dynamics is accurate to better than 2% at energies above the threshold for the first vibrational state.[14,15] This treatment does not affect the total e-H_2 cross section, which is dominated at low energies by elastic scattering.

Solution of the coupled integro-differential scattering equations proceeds via a new implementation of the integral equations algorithm, the details of which appear in a recent application to e-HF scattering.[17] In the present calculations we include enough terms in all eigenfunction expansions and control propagation of the scattering function so as to ensure convergence of all reported cross sections to better than 1%.

In Fig. 1 we compare the present crossed-beam and theoretical elastic and vibrational-excitation DCS at 1.25 eV. The excellent agreement over the angular range of the experiment seen here is typical of energies below 2.0 eV; at higher energies, the theoretical vibrational DCS is 15%–30% larger than experiment, mainly at angles between 10° and 80°. At 5.0 eV, above the peak in the integrated total cross section, the agreement is again excellent.

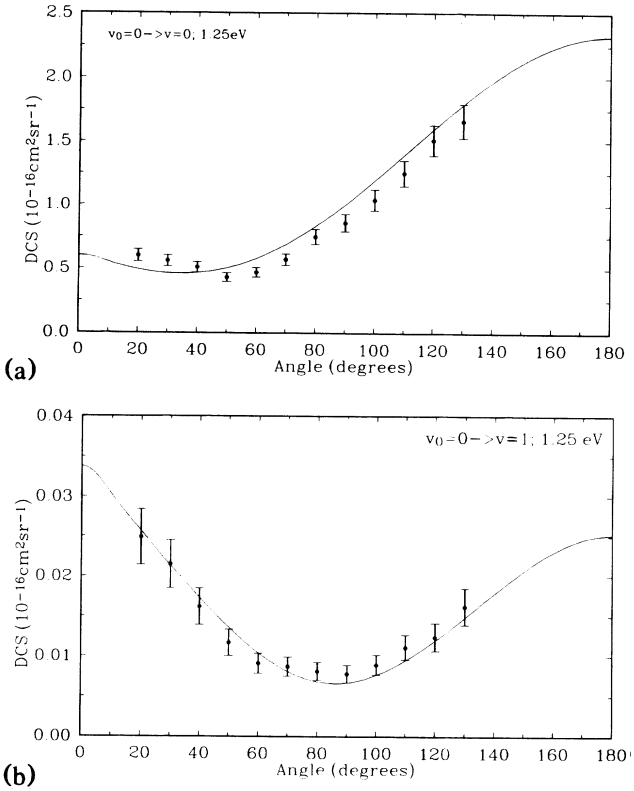

FIG. 1. (a) Elastic and (b) 0→1 vibrational-excitation e-H_2 differential cross sections from present measurements (solid circles) and calculations (curve).

In Fig. 2 we compare experimental and theoretical integrated 0→1 cross sections with those from previous beam experiments[5,6,18] and from the most recent swarm experiments.[19] Energies below 1.5 eV are particularly important because the accuracy of the swarm-derived $\sigma_{0\rightarrow 1}^{(v)}$ decreases rapidly as the energy increases above this value.[20] At and below 1.5 eV, the present crossed-beam result agrees very well with the theoretical cross section and with previously measured values[5,6] but is clearly incompatible with the swarm-derived cross section.

Above 1.5 eV, the present crossed-beam and theoretical cross sections differ by up to 25%; the earlier experimental results of Ehrhardt *et al.*[5] agree very well with theory at these energies, while those of Linder and Schmidt[6] agree with experiment. At present we cannot explain these differences. The major remaining approximation in the theoretical study is the use of a nonpenetrating approximation to short-range bound-free correlation effects,[21] but $\sigma_{0\rightarrow 1}^{(v)}$ is most sensitive to these effects at 1.5 eV, where agreement with experiment is excellent. Moreover, DCS are least sensitive to polarization and correlation around 80°, where the agreement with experiment is best.

The long-standing impasse between beam and swarm

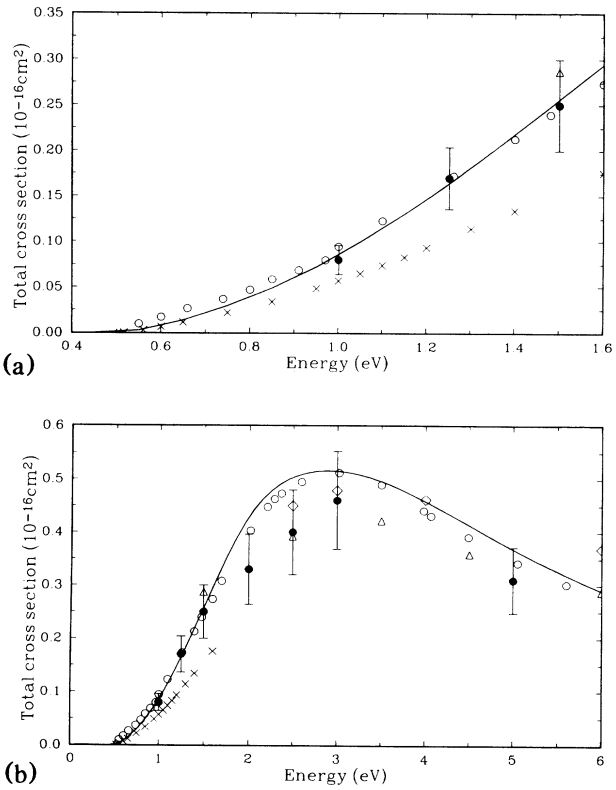

FIG. 2. Integrated $0 \rightarrow 1$ vibrational excitation e-H_2 cross sections for (a) 0.4 to 1.6 eV and (b) 0 to 6.0 eV from present calculations (curve) and various experiments: present (solid circles); Ehrhardt *et al.* (Ref. 5) (open circles); Linder and Schmidt (Ref. 6) (triangles); Nishimura, Danjo, and Sugahara (Ref. 18) (diamonds); and swarm derived (Ref. 19) (crosses).

techniques and between experiment and theory over the absolute value of $\sigma_{0\rightarrow 1}^{(v)}$ has centered on the crucial low-energy region below 1.5 eV, where several energy-loss processes compete and where the swarm-derived vibrational cross section is thought to be accurate provided the rotational cross sections are known. Notwithstanding residual differences between the present crossed-beam and theoretical cross sections at higher energies, we consider the present study to have settled this long-standing controversy. In particular, the present theoretical formulation, which combines vibrational close coupling, an adiabatic treatment of rotation, and a separable treatment of exchange, appears to accurately describe the $0 \rightarrow 1$ excitation at these energies. A critical discussion of the use of swarm analysis is beyond the scope of this paper and its authors, but we note that the present study has stimulated a new investigation of electron transport in H_2 by Monte Carlo methods.[22] We believe that our results also argue strongly for a rigorous study of the interplay of all the components of the swarm cross section set in the analysis of swarm data in order to clarify the level of uniqueness with which each is determined, and, perhaps, to obtain practical estimates of the errors inherent in them.

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