Experimental absolute differential cross section for the excitation of the lowest triplet state of [1.1.1]propellane by electron impact

Michael Allan

Articles you may be interested in

Experimental absolute differential cross section for the excitation of the lowest triplet state of [1.1.1]propellane by electron impact

Michael Allan

Institut de Chimie Physique, Université de Fribourg, Pérolles, CH-1700 Fribourg, Switzerland

Absolute differential cross sections for collisions of low-energy electrons with [1.1.1]propellane were measured. Presented are the energy dependence of the elastic cross section at 90° in the range 0.5–16 eV, energy dependence of the cross section for the excitation of the $^3A_2''$ lowest triple state at 90° up to 6 eV above threshold, and the angular dependence of the inelastic cross section at energies 1.5, 2.6, and 5.0 eV above threshold. The data is compared with the results of a recent *ab initio* scattering calculation [C. Winstead, Q. Sun, and V. McKoy, J. Chem. Phys. **97**, 9483 (1992)]. The calculated cross section is found to be about two times larger than the experiment in absolute magnitude and to reproduce qualitatively correctly the main experimental features both in the energy and the angular dependence.

INTRODUCTION

Knowledge of quantitative cross sections for electronic excitation of small polyatomic molecules is a key prerequisite for an improved understanding and modeling of low-pressure discharge plasmas which are often used in microelectrons fabrication and in surface treatment. The cross sections are further a valuable source of information on excited states, and on transient anions (resonances) and their decay dynamics. The interest in these cross sections has recently been promoted by advances in the capabilities of high-performance parallel computers and with the development of theoretical methods for electron–molecule scattering, making it possible to attempt detailed *ab initio* studies of the cross sections for fairly large polyatomic molecules. This development calls for a parallel advancement on the side of the experiment since quantitative experimental data, required to test the theoretical models, are often not available.

A recent example of this development is the measurement[1] and subsequent calculation[2] of the cross section for the excitation of the lowest triplet state in [1.1.1]propellane (structural formula is given in Fig. 1). This somewhat "exotic" hydrocarbon is a particularly valuable test case, because its "chromophore," responsible for resonance phenomena at low energies, is a stretched C–C single bond, and thus of a fundamentally different nature than the frequently studied π bonds in molecules like N_2 or ethene. The experimental spectrum of propellane given in Ref. 1 was only in relative units and was measured at a fixed scattering angle, however, permitting a comparison of only the shape of the energy dependence of the cross section with theory, but not of its absolute magnitude and angular dependence. The result was, despite the limited scope of the comparison, encouraging. In particular, both experiment and theory indicated a sizeable cross section enhancement caused by a core-excited shape resonance situated a few electronvolts above the excitation threshold. The present work extends the experimental study by presenting the absolute value and angular dependence of the cross section, permitting an in-depth comparison of experiment and theory.

EXPERIMENT

The hemispherical electron spectrometer and the procedure of calibrating its response as a function of the incident and residual energies on helium have already been described.[3] It is an essentially standard electrostatic spectrometer using hemispherical deflectors for electron energy selection, but careful choice of materials (molybdenum for optics, mostly titanium for structural elements), consequent computer control, and other technical details result in improved performance. The analyzer is rotatable from −3° to 135° with respect to the incident beam and the instrument measures differential cross sections. The beam source and analyzer are differentially pumped by a 160 mm diam diffusion pump, the collision region by a 400 mm diam diffusion pump. The sample was kept at −80 °C and its vapor introduced into the collision region as an effusive beam through a nozzle with 0.25 mm diam and about 0.3 mm long, kept at 80 °C. The resolution was set to 25 meV. Instrumental response function for elastic scattering has been determined with help of the helium elastic signal, the analyzer response function has been determined on the helium near threshold ionization continuum. All excitation functions and energy-loss spectra were corrected for the instrumental response function, under the assumption of the product rule described in Ref. 3. The angular dependence spectra were measured by
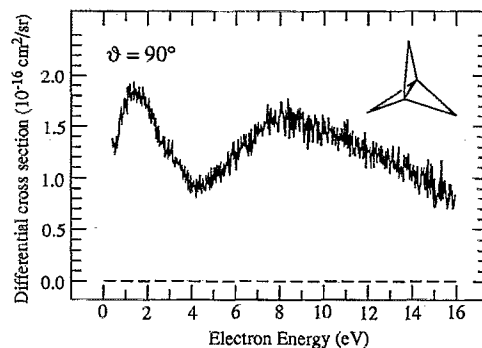

FIG. 1. Energy dependence of the absolute elastic differential cross section at 90° in [1.1.1]propellane.

repetitively scanning the analyzer position with a stepping motor. The response function with respect to the scattering angle has been calibrated on the helium elastic signal. The angular dependence spectra of inelastic signal were then corrected using an average of the response functions obtained at energies corresponding to the incident and residual energies. This procedure is justified by the fact that, for a well-tuned instrument, the angular response function is only weakly dependent on electron energy in the 2–20 eV range. The instrument is equipped with an absolute pressure gauge in the inlet system and absolute cross sections have been determined using the relative flow technique.[4]

RESULTS AND DISCUSSION

The first step of the present experiment is the determination of the absolute elastic cross section at a single point, at 90° and an incident electron energy of 7.36 eV. The measurement was performed using the relative flow technique described by Trajmar and co-workers.[4] Relative flows of helium and [1.1.1]propellane were derived from the rate of pressure rise in a fixed volume of 66 cm³, situated between the needle valve and the nozzle, when sample flow toward the nozzle was temporarily interrupted. The pressure behind the nozzle was kept sufficiently low during the absolute measurements (0.12 mbar for propellane, 0.13 mbar for helium) to operate essentially in the collisionless molecular flow regime within the nozzle exit aperture, avoiding errors due to viscous flow. The flows of propellane and helium were 0.12 and 0.53 mbar cm³/s, respectively. Elastic signal intensity of helium and (rotationally integrated) elastic signal intensity of propellane were then determined by repetitively scanning the elastic peaks and integrating under them. The cross section was then determined from the relative flows and signals, and the established theoretical cross section value for helium,[5] to be 1.52×10^{-16} cm²/sr ($\pm 25\%$) at this energy and scattering angle.

Figure 1 shows the energy-dependence of the elastic cross section, recorded at 90°. To obtain this curve, the elastic signal was corrected using a response function obtained by comparing the helium elastic signal with the theoretical reference,[5] and the spectrum was then normalized to the absolute value at 7.36 eV given in the preceding paragraph.

The ratio of elastic and inelastic signals were then determined with help of the "E-jump" experiment,[4] that is by recording an energy-loss spectrum with a constant incident energy of 7.36 eV whereby the elastic peak and the triplet band were scanned repetitively, skipping the uninteresting region between the two. The energy-loss spectrum was then corrected for the instrumental response function and is shown in Fig. 2. The vertical transition energy, 4.70 eV, agrees well with the value of 4.695 eV obtained with a different instrument in Ref. 1. The transition energy of the lowest vibronic level in Fig. 2, 4.19 eV, agrees well with the energy of the lowest vibronic level observed in Ref. 1 with a residual energy $E_r = 5.0$ eV. On the other hand the observation of an even lower vibronic level, at 4.09 eV, reported in Ref. 2 with $E_r = 2.7$ eV, could not be confirmed in this work. The present spectrum has been carefully calibrated, and a likely cause of the discrepancy in the position of the lowest
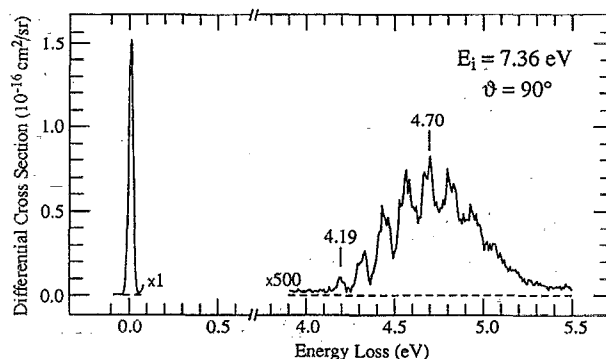

FIG. 2. Energy-loss spectrum recorded at 90° and at a fixed incident energy of 7.36 eV (on resonance), showing the elastic peak and the $^3A_2''$ band. The ratio of the areas under elastic peak and under the $^3A_2''$ band is used to determine the rovibrationally integrated $^3A_2''$ cross section at 90° and 7.36 eV.

vibrational level appears to be a rare instrumental problem during the measurement of the $E_r = 2.7$ eV spectrum in Ref. 1, an unstable electrical contact causing occasional eratic shifts in the electron accelerating voltage. The present value of the origin of the A_2'' band should thus be preferred. The spectrum in Fig. 2 is normalized to make the *height* of the elastic signal equal to the absolute elastic cross section. The height of the inelastic signal in Fig. 2 may thus be taken as vibrationally not integrated cross section. To obtain the vibrationally integrated cross section, required for the comparison with theory, the ratio of the areas under the elastic peak and the triplet band were taken and found to be equal to 66. The vibrationally integrated cross section for excitation of the triplet state at 7.36 eV is thus equal to the elastic cross section divided by 66, that is to 0.023×10^{-16} cm²/sr. The error limit is larger than for the elastic cross section because of the uncertainty in the correction for the response function, and is taken as $\pm 35\%$.

In the next step, the energy dependence of the cross section for the excitation of the triplet state is measured by recording the energy dependence of the signal at an energy loss of 4.68 eV, that is at the maximum of the triplet band, and correcting for instrumental response function as described above. The energy dependence of the vibrationally integrated cross section would have to be determined, strictly speaking, by recording the energy dependence curves for the individual vibronic levels of the triplet band (which have different threshold energies!) and summing them up. Since the calculation disregards the nuclear motion, and thus the different thresholds for the individual vibronic levels, it appears more appropriate, however, to take the energy dependence recorded at the maximum of the triplet band (i.e., the vertical transition) and normalize it to the vibrationally integrated absolute value of 0.023×10^{-16} cm²/sr at 7.36 eV. The resulting curve is compared with the theoretical result[2,6] in Fig. 3.

The calculated curve agrees with the experiment as far as qualitative features are concerned, both curves consist of a relatively narrow resonance band superimposed on a gradually rising background. These are two important quantitative discrepancies, however. First, the resonance is calculated at an energy about 2.75 eV higher than measured. This point
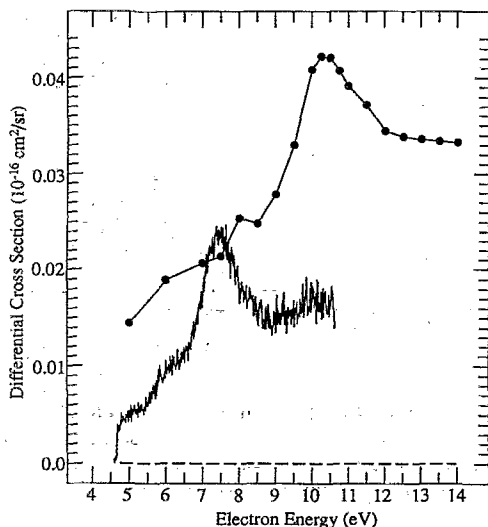
FIG. 3. Differential cross section for the excitation of the $^3A_2''$ band at 90° as a function of incident electron energy. Line with statistical noise is the experimental cross section, recorded at the maximum of the $^3A_2''$ (see Fig. 2), but normalized to reflect the rovibrationally integrated cross section. Large dots connected by straight lines represent the result of the calculation of Winstead et al. (Refs. 2 and 6).

has already been discussed and rationalized as a consequence of neglected target polarization in Ref. 2. The calculated cross section is further about two times larger than experiment in absolute magnitude. Both differences resemble the observation made while comparing results of calculation and of preliminary measurements in ethene.[7] The difference in absolute magnitude exceeds the error limit of the measurement and would appear to be due, at least in part, to approximations used in the calculation. A final remark concerns the weak shoulder around 6 eV in the experimental spectrum. This shoulder does not appear in the relative spectrum of Ref. 1, but the two spectra are not necessarily contradictory, since they were recorded at different scattering angles. On the other hand the small amount of sample did not permit a conclusive experimental verification of this feature. It can thus only be speculated whether this shoulder corresponds to the subsidiary peak at 8 eV, below the main resonance, in the calculated spectrum. This feature of the calculated spectrum is, interestingly, also prominent only in the vicinity of 90°.

Finally, Fig. 4 compares the measured and the calculated angular dependencies of the cross sections. The statistical noise of the experimental data is relatively large due to the small amount of sample available. Figure 3 indicates that it is not meaningful to compare the measured and calculated cross sections at the same energies because of the different position of the resonance in the two curves. Figure 4 therefore compares the cross sections at energies with similar relation to the energy of the resonance, where similar physics can be expected. The calculation is found to reproduce qualitatively correctly several features of the experimental curves. Below resonance, at around 6 eV, both experiment and theory show shallow maxima at 0° and near 90°, and a shallow minimum near 40°. Similarly above the resonance, at 9.68 eV in the experiment and at 12 eV in the calculation,
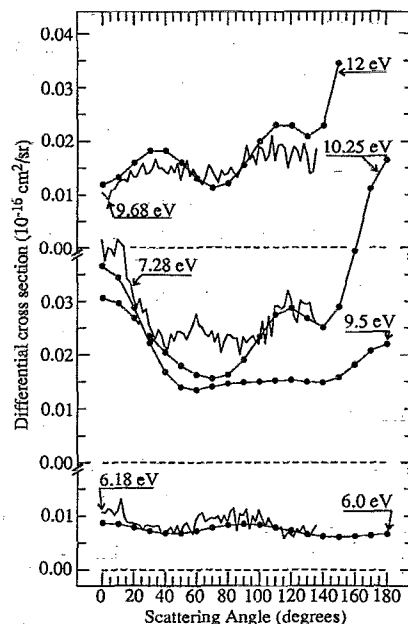

FIG. 4. Differential cross section for the excitation of the $^3A_2''$ band as a function of scattering angle. Lines with statistical noise are the experimental cross sections, recorded at the maximum of the $^3A_2''$ (see Fig. 2) and at incident electron energies given in the figure. They are normalized to reflect the rovibrationally integrated cross section. Large dots connected by straight lines represent the results of the calculation of Winstead et al. (Refs. 2 and 6), multiplied by a constant factor of 0.45 to permit a better comparison of the cross section shapes.

both experiment and theory show shallow maxima near 35° and 110°, and minima at 0° and near 70°. The variations of the theoretical cross section are more pronounced than in the experiment. The comparison at the energy of the resonance can be expected to be less satisfactory because the energy shift encountered in the calculation need not be the same for the resonance and the underlying background scattering. Both the cross section calculated on resonance and just below it are therefore shown for comparison in Fig. 4. The experimental and the "on-resonance" calculated cross sections agree as far as the peak near 120° is concerned. The calculated "below-resonance" cross section and experiment agree on a peak at 0° and a largely flat section around 60°.

In conclusion, the new experimental data presented here permits a detailed comparison of the recent *ab initio* calculation with experiment. The result is encouraging in view of the size of the theoretical problem. The absolute magnitude of the calculated cross section is within a factor of 2 of the experimental value. The calculation reproduces qualitatively correctly the shape of both the energy dependence and the angular dependence of the cross section.

ACKNOWLEDGMENTS

[1] O. Schafer, M. Allan, G. Szeimies, and M. Sanktjohanser, J. Am. Chem. Soc. 114, 8180 (1992).

[2] C. Winstead, Q. Sun, and V. McKoy, J. Chem. Phys. 97, 9483 (1992).

[3] M. Allan, J. Phys. B 25, 1559 (1992).

[4] J. C. Nickel, P. W. Zetner, G. Shen, and S. Trajmar, J. Phys. E 22, 730 (1989).

[5] R. K. Nesbet, Phys. Rev. A 20, 58 (1979).

[6] V. McKoy and C. Winstead, private communication.

[7] M. Allan, invited talks of the 18. ICPEAC satellite symposium on electron collisions with molecules, clusters, and surfaces (University of London 1993), in print.