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Positron resonances in vibrational excitation

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Scattering resonances are relatively rare in positron scattering, with the only observed instances to date being vibrational Feschbach resonances, observed through their effect on the annihilation cross section. In this study, we present observations of resonances in vibrational excitation by positron impact on ethane, ethylene, and acetylene, and explore the dynamics of positron resonance formation and decay. There are far fewer resonances observed in the excitation spectra than in the annihilation channel. Due to the difficulties inherent in measuring relevant scattering processes at the low energies required to observe the resonances, the formation and decay modes of these resonances are still not well understood. Theory suggests that intramolecular vibrational energy redistribution plays a key role in resonance formation and decay, which should lead to enhancement of the vibrational excitation cross sections in the region of the resonance energies. These results demonstrate that further work is required to fully understand these systems.

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I. INTRODUCTION

Scattering resonances provide a platform to explore the effect of correlations in quantum systems, and have been widely observed in many systems [1,2]. They are responsible for the enhancement of key cross sections that give rise to key technologies [3] and even the basic building blocks of life itself [4]. The theoretical problem is notoriously difficult to address, with few *ab initio* calculations able to reliably reproduce the experimental observations of resonances in systems such as low energy electron scattering. As such, the study of scattering resonances is still an active area of research.

In the case of positron scattering, such resonances were not observed until relatively recently [5], in contrast to the case of the scattering of their matter counterpart, the electron [6]. This is partly due to the positive charge of the positron, which results in a repulsive interaction with the net static Coulomb potential of atoms and molecule, once it is in close proximity to the target. However, there have been extensive observations of vibrational Feshbach resonances (VFR) in positron scattering from a broad range of hydrocarbon molecules, observed through significant enhancement to the annihilation cross section, usually expressed as the parameter Z_{eff} [7]. These observations have been interpreted as evidence of the existence of positron bound states for the molecules in which they have been observed, and the downwards shift in energy from the vibrational excitation threshold as a measure of the binding energy of the positron to the ground state molecules. Theoretical calculations have provided a framework for understanding the formation and decay of these resonances in terms of intramolecular vibrational energy redistribution, where after capture into a resonant state the excess energy is distributed amongst the various vibrational modes of the molecule, which must then "rephase" before the positron is ejected [8,9]. This leads to a long dwell time for the positron on the molecule, and consequently enhances the annihilation cross section. A consequence of this understanding is that the resonance can also decay via vibrational excitation of low lying vibrational modes of the target, which leads to an expectation of enhancement of these excitation cross sections at resonant energies. Enhancement has been observed previously in this manner for many resonance scattering phenomena (see, e.g., [1,2]). In this paper, measurements of vibrational excitation for ethane, ethylene, and acetylene are presented, with the aim of exploring our understanding of the formation and decay of these resonances.

II. EXPERIMENT

Experiments were undertaken using the positron beamline at the Australian National University. This apparatus has been described in detail previously [10], so only brief details will be presented here. Positrons are obtained from a ^{22}Na radioactive source, and then moderated using solid neon to provide a low energy positron beam, confined radially using a strong magnetic field (approximately 500 G). This beam is directed into a Surko trap system [11], which traps and cools the positrons before releasing them as a pulsed, low-energy positron beam [12], with an energy spread of 50 meV (FWHM), and tunable to the desired interaction energy. The beam is directed to a target cell of well-defined length which contains the target species of choice. Pressure in the cell is controlled using a needle valve and measured to high precision and accuracy with a capacitance manometer. After transition through the cell, the beam is directed to a retarding potential analyzer and microchannel plate detector system, which can measure the parallel energy distribution of the beam after interaction with the target [13]. Through an understanding of the motion of the positrons in a magnetic field, and using the pressure and length measurements from the scattering cell, absolute cross sections can be obtained for a range of scattering processes

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[14]. This was previously demonstrated for the measurement of vibrational excitation cross sections [15], and is used here to measure vibrational excitation, as well as total scattering cross sections, in the energy range from 100 to 800 meV. Absolute cross section values are presented here; uncertainty in the values arises primarily from errors in determining the pressure in the cell and statistical errors in the measurement. For the measurements presented here, the primary contribution is from statistical uncertainty. In the case of the total cross sections, some contribution from the forward scattered positrons is missed, due to the inability to discriminate forward scattered positrons from the primary beam in the guiding magnetic field. This is discussed further below, in the context of these results. Vibrational excitation measurements do not suffer from the same angular discrimination issues, thanks to the additional total energy loss involved in the scattering. Thus the cross sections presented here represent the true magnitude of the total vibrational excitation cross sections.

Cross sections were measured for positron scattering from ethane, ethylene, and acetylene. The molecules were chosen because of their relatively simple structure, which allows for separating out the fundamental vibrational modes with the current experimental energy resolution. The annihilation cross section has been previously measured for all three molecules with significant differences in the resonance structures observed. In particular, ethane has a prominent resonance clearly associated with the C-H stretch mode of the molecule, which is smaller in ethylene and disappears entirely in the case of acetylene. In contrast, acetylene has a strong resonance feature at approximately 100 meV, the energy of the lowest lying vibrational fundamental mode (C-H rocking), which is smaller in ethylene and absent in the case of positron scattering from ethane. The changing nature of the resonance structure in each molecule is suggestive of a change in the primary decay mode between annihilation and ejection of the positron. This might suggest that an enhancement of the vibrational excitation channels could be expected, given the expected role of vibrational energy redistribution. Vibrational mode energies were taken from [16,17].

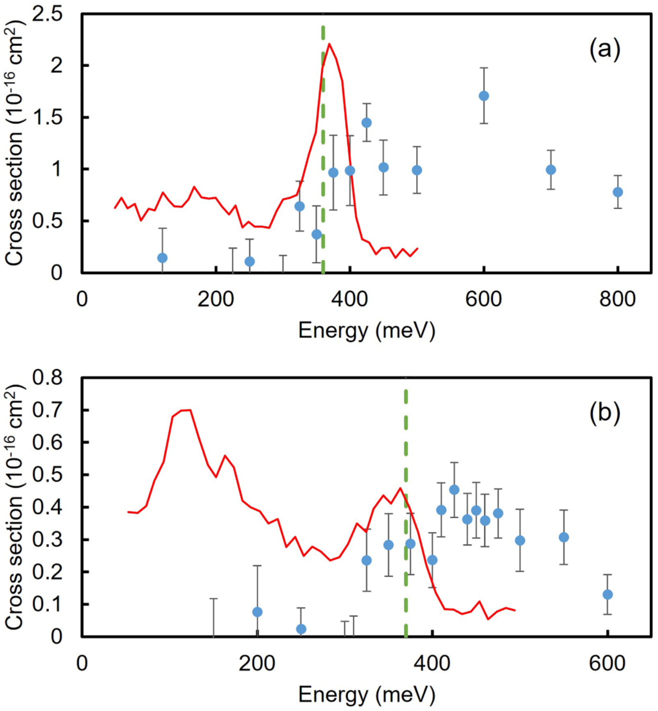

FIG. 1. Positron excitation of the C-H stretch vibrational mode of (a) ethane, (b) ethylene. Blue points are the experimental data, and the red solid line is the annihilation data from [18], scaled to fit to the vibrational excitation cross section measurements. The dashed vertical line indicates the threshold for the excitation in each molecule.

III. RESULTS AND DISCUSSION

The results are presented according to the vibrational mode measured in each molecule. Figure 1 shows the excitation of the C-H stretch mode for ethane and ethylene; no excitation of this mode was observed in the case of acetylene. Our measurements are compared to the annihilation (Z_{eff}) measurements of Young and Surko [18]. The annihilation data have been scaled to make a meaningful comparison, given that there are orders-of-magnitude of difference in the corresponding cross section values. The threshold for excitation for this mode is 360 meV in the case of ethane and 370 meV for ethylene, with dipole active modes in each case. As such, excitation via positron impact is allowed. The resonance feature previously observed in the annihilation spectra for each molecule, associated with this vibrational mode, overlaps the onset of the vibrational excitation, as can be seen in Fig. 1. It might therefore be expected to result in some enhancement of the cross section at threshold. However, in the case of ethane and ethylene, the cross section for excitation increases smoothly from threshold to maximum values of ≈ 1.0 and $\approx 0.4 \times 10^{-20}$ m^2, respectively, with no evidence of resonant enhancement. The relative magnitudes of the cross sections might be expected (with ethane being larger than ethylene), as ethane has six C-H bonds compared to ethylene's four. In the case of acetylene, there was no observed resonance associated with the C-H stretch mode (at 407 meV and dipole allowed) in the annihilation measurements, and also no measurable excitation of this vibrational mode in the present work.

Figure 2 shows the measurements for the excitation of the C-C stretch mode in ethylene and acetylene, again compared with the annihilation data of Young and Surko [18]. Measurements for this mode in ethane were not possible, due to the low excitation threshold of 123 meV, and slightly worse energy resolution for this series of measurements. In this case, the mode is not dipole active in either of the target molecules, so cannot be excited in a direct collision process. However, if vibrational redistribution of the resonance energy is present, we might expect to observe excitation at the resonance energies in each case. In the case of ethylene, there is some indication of a nonzero cross section in the region from threshold (at 201 meV) to 300 meV impact energy, but given the error bars on the experimental data it is not possible to be more conclusive. This does not correspond with any resonances in the annihilation spectrum. By contrast, there is a clear excitation of this mode in acetylene (with a threshold energy of 245 meV), which is suggestive of some resonance enhancement in the threshold region. This corresponds closely

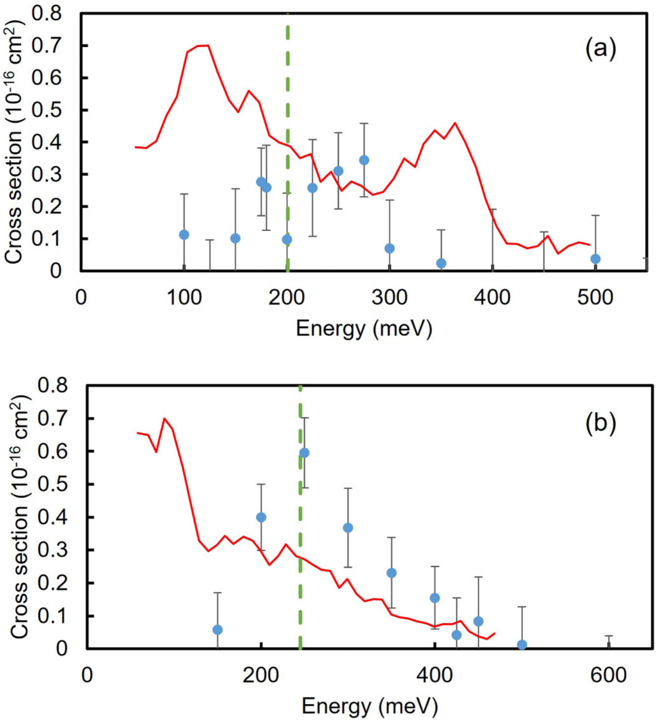

FIG. 2. Positron excitation of the C-C stretch vibrational mode of (a) ethylene and (b) acetylene. Blue points are the experimental data, and the red solid line is the annihilation data from [18], scaled to fit to the vibrational excitation cross section. The dashed vertical line indicates the threshold for the excitation in each molecule.

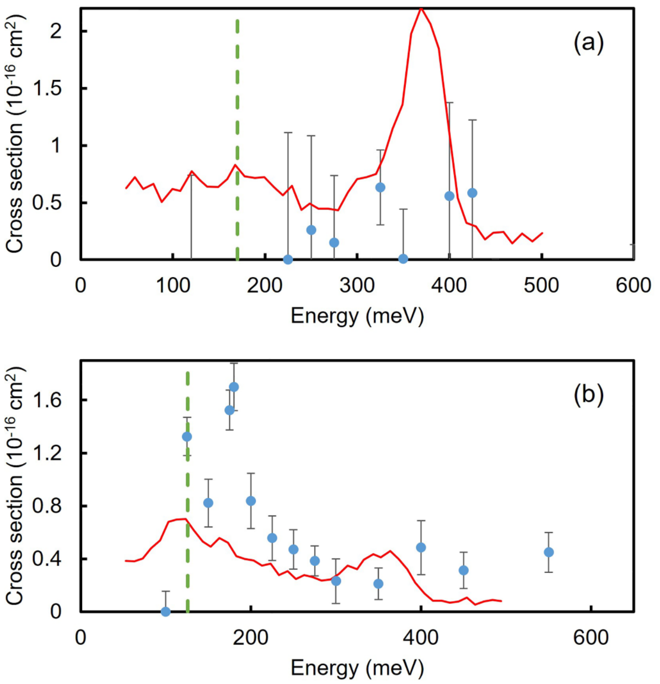

FIG. 3. Positron excitation of the C-H_3 and C-H_2 deformation modes of (a) ethane and (b) ethylene, respectively. Blue points are the experimental data, and the red solid line is the annihilation data from [18], scaled to fit to the vibrational excitation cross section. The dashed vertical line indicates the threshold for the excitations in each molecule.

to the relative shape of the annihilation data, which also has suggestions of a resonance at around 230 meV.

The final vibrational mode excitations that could be resolved using our present experiment were CH_2 (ethylene) and CH_3 (ethane) deformation modes, with threshold energies of approximately 150 and 127 meV respectively. There are several mode excitations possible at around these energies, and the individual modes are not resolvable using the current experiment. As a result, the data presented here is the sum over four mode excitations from 126 to 179 meV in ethylene, and four modes between 170 and 182 meV in ethane, with a mix of dipole active and inactive modes in each target. In the case of acetylene, with only single CH bonds, these deformation modes are not present. The data for these measurements are presented in Fig. 3.

In the case of the ethane data, there is no measurable excitation of these vibrational modes, to the limit of the current measurements. However, the ethylene data show relatively strong excitation of the vibrations in this energy range, with a peak in the data corresponding to a small resonance structure at approximately 170 meV in the annihilation cross section measurements. There is also a very strong onset of the excitation at the threshold of 130 meV, which overlaps the biggest resonance peak in the annihilation data. Notably, there are no structures in the vibrational excitation that correspond the the resonances seen in the annihilation just below 400 meV in each molecule.

Considering the measurements as a whole, there is only clear evidence for resonant structure in two of the measurements: the C-C stretch mode excitation in acetylene and the CH_2 modes of ethylene. While we see excitation of the C-H stretch modes in both ethane and ethylene, there is no obvious resonance enhancement due to the overlap with the broad resonance seen in the annihilation cross section measurements of Young and Surko [18]. It is notable that in at least one of these cases—the C-C stretch mode excitation in acetylene—the mode is dipole inactive and can only be excited by positrons through some intermediate process, such as resonance formation. This offers evidence of a previously unobserved resonance in the positron scattering from this target.

Overall, there is less vibrational energy redistribution and decay into vibrational modes than might be expected for the current group of targets, given the current best understanding of the formation and dynamics of these resonances. In the model of resonance formation and decay presented by Natisin *et al.* [19], they state that "the positron annihilation rate in the VFR is significantly smaller than the detachment rate due to vibrational deexcitation." This suggests that there should be a prominent presence of resonance structures in the vibrational excitation cross sections, something in contrast to what has been observed in the present experiments. There is only one remaining channel for the decay of these resonances, which is through elastic decay of the resonance complex. To investigate this, low energy measurements of the total positron scattering cross sections were also made for each molecule. It should be noted that the techniques outlined in [14] were again used, but, due to the energy resolution and the low incident energies, the

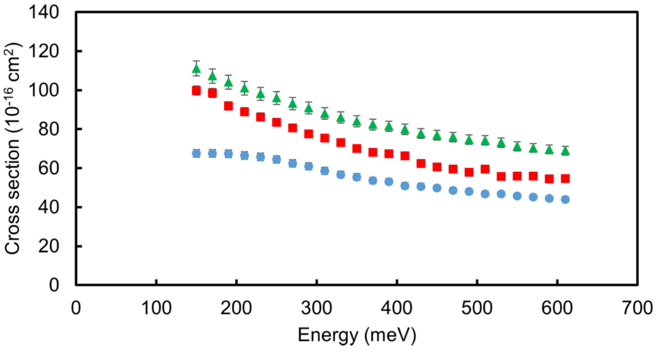

FIG. 4. Low energy positron scattering total cross sections for ethane (blue circles), ethylene (red squares) and acetylene (green triangles). Error bars are absolute, and dominated by statistical error. The cross sections miss a significant portion of the forward angle scattering of the positrons, but are still assumed to be sensitive to the presence of any resonance features. A 10 Å offset has been added to the acetylene data to allow for a qualitative comparison between the three measurements.

effective integration of the scattering is over a finite angular range, as opposed to scattering from 0° to 180°, as previously detailed [20]. In this case, the measurements are not a true total cross section, as they will exclude a significant portion of the forward (and backward) angle scattering, but if there is a strong resonance feature, we would expect it to still be present in the measurement. It should also be noted that the measurements include elastic, vibrational, and rotational excitation.

Figure 4 shows the measured total cross section data for the three targets, with an offset in the acetylene data for clarity of comparison. With a large fraction of the forward angle scattering missed in the measurement (ranging from about 40° at the lowest energies to 20° at 0.6 eV), qualitative comparison is the only relevant way to interpret the data and the cross section magnitude is only a rough guide in this case. Given the measured vibrational excitation cross sections (at $\approx$1% of the total), the cross sections are seen to be dominated by contributions from elastic scattering (integrated over rotational excitations). It can be clearly seen that there are no resonance features in the cross section measurements, which span the energy range of the resonances observed in the annihilation measurements. The slight flattening of the ethane cross section at low energies is due to slightly worse angular resolution than in the other cases (see [20] for further details on this effect). Coupled with the the fact that only a few of these resonance features are evident in the vibrational excitation channels of the molecules studied, this would seem to contradict the current expectations of resonance dynamics and decay. Indeed resonances, at least for these relatively small molecules, appear most prominently in the annihilation channel, while there is less evidence than expected of intravibrational energy redistribution (IVR) leading to decay into vibrational states of the neutral molecules.

It should be noted, however, that there is some evidence of IVR that arises from these measurements. In particular, the CC stretch modes of the molecules cannot be excited through the dipole interaction, which would be expected to be the main means of excitation in the absence of resonances. The fact that this mode is clearly excited in acetylene, in the region in which enhancement is observed in the annihilation measurements, is a clear signature that IVR and decay into vibrationally excited states at least plays some role in the formation and decay of these scattering complexes. It should also be noted that this resonance is not observed in the annihilation data. The same can be said of the vibrational excitation of ethylene, for the collection of modes that are able to be excited from 130 to 180 meV. The fact that there is prominent excitation from the threshold of the lowest mode, which is also dipole inactive, is another signature of vibrational energy redistribution.

Despite these arguments, it is clear that our understanding of the resonance formation and decay picture remains incomplete. There is no observed presence of the most prominent resonance in positron annihilation on ethane, which is associated with the C-H stretch modes of the molecules, in either the excitation of lower lying vibrational states or the elastic channel. It may be that the resonance itself is relatively weak and long lived, leading to decay predominantly by annihilation, with no (or minimal) free positron escape through the decay of the complex state. The same can be said for many of the other previously observed resonances for the three targets investigated as a part of this study.

IV. CONCLUSION

This paper has presented an investigation of the vibrational excitation of a series of simple hydrocarbon molecules, each containing two carbon atoms, with the aim of exploring the dynamics and decay of positron scattering resonances previously observed in Z_{eff} measurements [18]. We have observed several resonances, including one that, to our knowledge, has not previously been observed in annihilation measurements. It should be noted that, given the 50 meV energy resolution of these measurements, resonances with smaller widths than this may be difficult to be observe with the measurements presented here. We note that previous resonance features observed in the annihilation cross sections have widths comparable to, or greater than, 50 meV. As a result, in light of previous theoretical modeling of the process of resonance formation and decay [19], we have observed surprisingly little evidence of the resonances in alternative decay channels. The measurements clearly support the concept of IVR playing a role in the process, with the excitation of dipole forbidden modes observed and features that can be associated with some of the previously observed features of the Z_{eff} spectra. However, it appears that there is considerably more work to be done to fully understand these resonances, given the absence of signatures of some of the largest Z_{eff} features in either vibrational excitation or elastic scattering. Given that there have been observations of these features in positron annihilation on a large range of hydrocarbon (and substituted hydrocarbon) molecules, further experimental and theoretical investigations are clearly justified.

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