J. Phys. Chem. A **2009,** *113,* 14251–14254 **14251**

Low-Energy Positron Scattering from Dihydropyran[†]

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Received: March 19, 2009; Revised Manuscript Received: April 14, 2009

We report on total cross section measurements for positron scattering from dihydropyran (C_5H_8O), with the energy range of the present study being 0.15−48 eV. To the best of our knowledge, there are currently no other corresponding experimental data or theoretical computations against which we can compare our results. The effect of this species' important dipole moment and significant dipole polarizability on the scattering dynamics is considered, as is the opening of the positronium formation channel.

Introduction

In chemistry, particularly organic chemistry, structurally related molecules are often studied to better understand corresponding trends in their chemical activity. Such studies are not so prevalent in physics, although we note the extensive positron annihilation work on the alkane (C_nH_{2n+2}) homologous series[1] for which the observed structures are now understood in terms of vibrational Feshbach resonances. Further work, consistent with this theme, by the San Diego group for positron annihilation in the fluorinated methane series CH_nF_{4-n} is also worthy of note.[2] Corresponding positron−molecule scattering studies, in which total cross sections (TCSs) for a series of structurally related species are determined, are much more limited. In this respect we note data from the earlier review by Kimura et al.[3] and the more recent work of Zecca et al.[4]

Here we report results for total cross sections for positron scattering from dihydropyran (C_5H_8O). This represents the second species we have investigated in the series of cyclic ethers shown schematically in Figure 1, with the first molecule considered having been tetrahydrofuran (THF).[5] Note that this series is not a homologous series, but it is clear from Figure 1 that all the molecules are structurally related to a high degree. Indeed all the cyclic ethers of Figure 1 are used as important solvents, as chemical intermediates, or as the monomer for ring-opening polymerization. Each possesses a sterically unhindered oxygen atom that carries two unshared pairs of electrons, which are expected to play an important role in their physicochemical behavior. In addition, we note that oxirane, oxetane, THF, and dihydropyran each possess a strong permanent dipole moment and significant dipole polarizabilities. We have previously seen in our positron (e^+)−formic acid,[6] e^+−THF,[5] and e^+−3-hydroxy-THF[7] TCS work that molecules having a strong dipole moment and/or significant dipole polarizability will cause the dynamics of the scattering process to be significantly affected. We also anticipate that such behavior will again be observed, and to help elucidate these effects, we will make a detailed comparison between the present e^+−dihydropyran TCS results and those obtained previously for e^+−THF scattering. Finally, we note that, in spite of the importance of this molecule in biological processes,[8] there appears to have been no previous experimental or theoretical studies into the scattering of either positrons or electrons from dihydropyran.

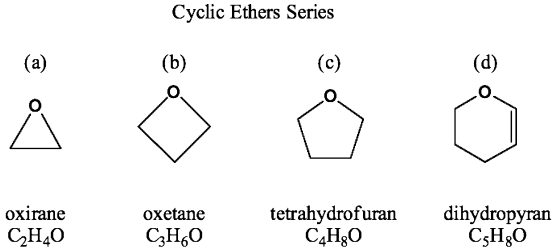

Figure 1. Schematic diagram illustrating the structures for relevant members of the cyclic ether series, and in particular dihydropyran.

In the next section of this paper we briefly describe our experimental apparatus and measurement techniques. Thereafter, total cross section results for positron scattering from dihydropyran are presented and discussed, before some conclusions are drawn.

Experimental Apparatus and Measurement Techniques

The positron spectrometer (see Figure 2) used at the University of Trento was developed by Zecca and co-workers and has been described in detail elsewhere.[9] We therefore do not repeat those details again here, except to note that a tungsten moderator is employed in conjunction with a radioactive ^{22}Na isotope (∼3 mCi) and some electrostatic optics to produce our positron beam. We also highlight that it is standard practice, as a check of the validity of our techniques and procedures, to perform periodical measurements with molecular nitrogen (N_2). N_2 was chosen as a benchmark because of the availability of a reliable set of data from Hoffman et al.[10] and also because very accurate (unpublished) data have been measured in our laboratory which are in excellent accord with those of Hoffman et al.

The basis of all our linear transmission experiments is the Beer−Lambert law, as defined by

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[†] Part of the "Vincenzo Aquilanti Festschrift".

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10.1021/jp9024602

$$I_1 = I_0 \exp\left(\frac{-(P_1 - P_0)L\sigma}{kT}\right) \tag{1}$$

where I_1 is the positron beam count at P_1, the pressure measured with the species of interest routed to the scattering cell, k is Boltzmann's constant, T is the temperature of the gas (K), σ is the total cross section of interest, I_0 is the positron count rate at P_0, the pressure with the gas diverted into the vacuum chamber, and L is the length of the scattering region.

For a physical application of eq 1, several crucial precautions should be taken and care must be exercised during the measurements. Those considerations include minimizing double-scattering events and ensuring the TCSs are pressure independent. In addition, only a high-purity target dihydropyran sample (Aldrich, >97%) was used in the present measurements, and this sample was subjected to several freeze−pump−thaw cycles to ensure it was appropriately degassed. Note that while the boiling point of dihydropyran is 89 °C, it is volatile enough at room temperature to provide a practical source without further heating.

The geometrical length of the scattering region is 22.1 ± 0.1 mm, with apertures of 1.5 mm diameter at both the entrance and exit of the scattering chamber.[9] End effects were considered in all our studies; however, it is well-known that such effects cancel[11] if both apertures have equal diameters as in our case. As a consequence we believe their contribution to the uncertainty in the value of L is likely to be less than 0.2% here. In our application of eq 1, the value of L used is always corrected to account for the path increase caused by the gyration of the positrons in the focusing axial magnetic field (~8−10 G) present in the scattering region. This correction was ~5% on L in this work. The gyration of the positrons can also potentially increase the angular resolution error compared to that of the no-field case.[12] This can also be corrected for, provided appropriate differential cross sections are available. Unfortunately, such differential cross sections are typically unavailable so that the TCSs we report represent a lower bound on the exact values. Since our angular resolution depends on the energy of the positrons, we anticipate that our angular resolution error could be on the order of a few percent at energies higher than a few electronvolts. Below a few electronvolts this angular resolution error would possibly increase and perhaps be as high as 10−20%, depending on the detailed behavior of the differential cross section of the dihydropyran molecule under study.

It is very important for the energy scale to be calibrated accurately. The zero for the energy scale, in the absence of the target gas, was determined in this work with a retarding potential analysis of the beam.[13] This measurement suggests a probable error of typically ±0.2 eV in our energy scale, and an energy width of the positron beam of ~0.3 eV (fwhm). It is also crucial to accurately measure the scattering cell pressure, which we achieve with an MKS Baratron capacitance manometer. Here, thermal transpiration corrections (~3% at worst) to the pressure readings are made using the model of Takaishi and Sensui.[14]

Finally, we note that the data collection and analysis codes were driven by software developed at the University of Trento, for application on a personal computer. The positron energy range of our current total cross section measurements was 0.15−48 eV, with the absolute errors on our TCSs typically being within the range 5−15%. All our measurements were taken under stable positron beam conditions.

Results and Discussion

In Table 1and Figure 3 we show the present total cross section results for positron scattering from dihydropyran. Note that the errors in Table 1 are simply the statistical uncertainties on our work, rather than the overall error on the TCSs at a given energy, as given above. It is clear from Figure 3 that the total cross section rises significantly in magnitude as the incident positron energy decreases. This behavior is consistent with dihydropyran having both a strong dipole moment (~1.38−1.48 D)[15,16] and also a large dipole polarizability (9.62 × 10^{-24} cm^3),[17] and is similar to what we saw previously in our work on formic acid.[6] Note that we have checked the validity of these values for the dipole moment and dipole polarizability by performing simulations using Gaussian software[18] with a B3LYP/6-31G model chemistry. These calculations gave a value of 1.70 D for the dipole moment and 8.726 × 10^{-24} cm^3 for the dipole polarizability, consistent with the earlier data.[15−17] While it is true that the rate of increase in the TCSs appears to diminish at around 0.4 eV, this observation simply reflects the effect of our finite energy resolution at these very low energies on the measured TCSs.

In Figure 3, we also attempt to determine the positronium formation threshold from our TCS results. To this end, lines of best fit, which seek to highlight at about what energy the monotonic decrease in the TCSs with energy changes slope, are plotted. Note that those very low energy points which are affected by the convolution caused by our energy resolution are excluded from this analysis. In this case, Figure 3 indicates that the slope is seen to change at ~2.1 ± 0.6 eV, where the rather large uncertainty here simply reflects the sensitivity of this determination to the actual choice of points included in our analysis. We have found two values for the first ionization potential (V_i) of dihydropyran in the literature.[19,20] The most recent from Stone and Lin[19] gives a value of 8.34 eV. This work

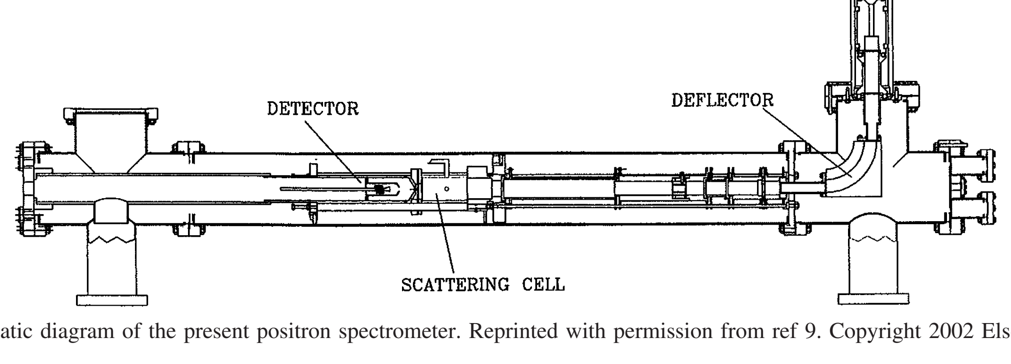

Figure 2. Schematic diagram of the present positron spectrometer. Reprinted with permission from ref 9. Copyright 2002 Elsevier.

TABLE 1: Present Total Cross Sections (10^{-16} cm^2) for Positron Scattering from Dihydropyran[a]

positron energy (eV)	cross section (10^{-16} cm^2)	error (10^{-16} cm^2)
0.15	146.0	11.4
0.20	142.5	7.6
0.25	120.7	11.7
0.30	117.5	8.9
0.35	109.4	2.0
0.40	119.7	12.5
0.45	116.0	9.9
0.50	116.7	4.4
0.55	115.1	1.8
0.65	97.3	1.6
0.75	91.1	4.8
1.00	79.9	4.9
1.25	72.2	2.5
1.45	70.7	3.2
1.50	69.3	2.6
2.00	57.8	0.2
2.75	54.4	7.7
3.00	43.5	3.3
4.00	42.6	0.4
4.75	43.3	0.8
6.75	39.6	2.3
9.75	31.8	1.4
11.75	32.8	1.7
13.75	30.1	1.2
15.75	32.6	2.2
17.75	32.2	0.9
19.75	30.1	1.6
25.75	30.6	1.1
28.00	29.8	0.8
30.00	27.1	0.1
32.00	29.1	0.7
34.00	27.1	0.2
36.00	26.4	0.9
38.00	26.2	0.4
40.00	27.5	0.2
42.00	26.7	1.5
44.00	26.5	0.3
46.00	25.8	1.2
48.00	26.0	0.6

[a] The errors given represent 1 standard deviation on the measured cross section at a given energy.

is, however, at a lower resolution than that of Planchaert et al.,[20] who found a vibrational series of peaks in the range 8.35−8.85 eV for ionization from the highest occupied molecular orbital of dihydropyran. Taking the centroid value of those peaks as a reasonable representation for the first ionization potential, our preferred value becomes $V_i = 8.6 \pm 0.2$ eV. As the general rule[1] is that the positronium threshold energy (E_{Ps}) for a given species can be obtained from

$$E_{Ps} = V_i - 6.8 \text{ eV} \tag{2}$$

we find that $E_{Ps} = 1.8 \pm 0.2$ eV. This value for the positronium threshold is largely consistent with that determined from Figure 3, so that the energy where the TCS changes slope is likely to be indicative for the positronium channel becoming open. Note that we have had consistent results using this approach for all molecules we have studied, including THF,[5] formic acid,[6] and 3-hydroxy-THF.[7] It is also manifest from Figure 3 that the opening of this positronium channel has an important effect on the magnitude of the TCSs above the threshold energy.

Finally (again see Figure 3), we compare the present e$^+$−dihydropyran TCS to that for the structurally related cyclic ether tetrahydrofuran. Recall[21] that the dipole moment of THF is ~1.63 D, while its dipole polarizability is ~6.97×10^{-24} cm^3. Thus, while the dipole moment of THF is a little larger than that for dihydropyran, its dipole polarizability is significantly smaller than that of dihydropyran. To first order, these observations and the different positronium threshold energies ($E_{Ps}^{THF} \approx 3.7$ eV) of the two species largely explain the observed comparative behavior of their TCSs. Namely, at energies below about 1 eV the effects on the scattering dynamics of the respective dipole moments and dipole polarizabilities largely compensate for one another, so that the TCSs are almost identical. At energies between ~1 and 1.8 eV, the TCS for dihydropyran starts to become a little stronger in magnitude compared to that for THF. This probably indicates that the dipole polarizability is starting to play a more predominate role in the scattering dynamics. Between 1.8 and 3.7 eV, the positronium channel for dihydropyran is open while that for THF remains closed. Hence, it is not too surprising that within this energy range the difference between the TCS for e$^+$−dihydropyran and that for e$^+$−THF scattering starts to increase. However, with the opening of the positronium channel in THF at 3.7 eV the difference in magnitude (recall Figure 3 is a log−log plot), between the TCSs as a function of energy for the two species, becomes almost a constant factor thereafter.

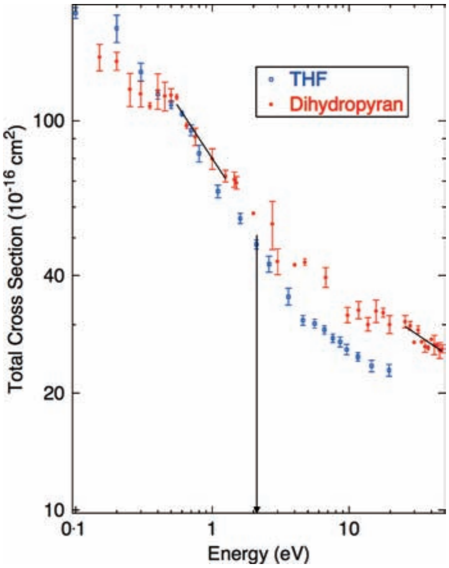

Figure 3. Present TCSs (10^{-16} cm^2) for positron scattering from dihydropyran (●). Also shown are the corresponding positron−THF TCSs from Zecca et al.[5] (□). Note the log axis scales.

Conclusions

We have reported results from an experimental study into positron scattering from dihydropyran. The important role played by both polarization and the permanent dipole moment of C_5H_8O in the scattering process was manifest. The present experimental results also clearly indicated the importance of the opening of the positronium channel on the reaction. Nonetheless, an ab initio quality theoretical study of this system could only further improve our understanding of its collision dynamics.

Acknowledgment. This work was supported under a Memorandum of Understanding between the University of Trento and the Flinders University node of the ARC Centre for Antimatter-Matter Studies. Financial support from DIISR through its International Science Linkages (ISL) scheme is also acknowledged. D.S. and M.C. thank the International Centre for

Theoretical Physics—TRIL Programme (Italy) for supporting their respective stays in Trento. M.C. also gratefully acknowledges the CSIR, Government of India, for providing additional financial assistance. S.C. thanks the Physics Department at the University of Trento for its financial support. Finally, L.C. thanks the Provincia Autonoma di Bolzano (Italy) for financial support. We all gratefully acknowledge the assistance of Dr. L. Campbell with the preparation of this manuscript.

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JP9024602