

## Excitation of Molecular Vibrations by Positron Impact

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Absolute cross sections for the vibrational excitation of CO, CO<sub>2</sub>, and H<sub>2</sub> by positron impact are presented for incident positron energies from 0.5 eV to several electron volts. The measurements use a novel technique that exploits the adiabatic motion of a positron beam in a strong magnetic field. This work is the first systematic experimental study of vibrational excitation by positron impact, and extends to energies where positron measurements have traditionally been difficult. The measured cross sections are compared with available theoretical calculations.

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Atomic and molecular physics using positrons is an active area for both experimental and theoretical research [1–5]. These studies are important in understanding the fundamental interaction of positrons with ordinary matter, including questions of positron attachment to atoms and molecules and positron-induced ionization [6]. They also have implications for research in other areas, such as the characterization of materials and material surfaces [7,8]. Experiments to date, however, have generally been restricted to incident positron energies of  $\geq 1$  eV. This is primarily due to the relatively poor energy resolution of moderated positron beams (especially compared to electron beams of the same energy). As a result, the only low energy ( $< 1$  eV) measurements to date have been for total scattering cross sections [9–11], with the exception of one differential elastic and one total vibrational cross section measurement [4].

The buffer-gas positron accumulation technique made available for the first time a source of positrons capable of high brightness and with an energy resolution comparable to typical electron beams [12]. In this Letter, we describe the use of an accumulator, in conjunction with an apparatus designed specifically for atomic and molecular physics experiments, to undertake a comprehensive study of vibrational excitation of molecules by low-energy positron impact. The experiments take advantage of the properties of the magnetized positron beam from the accumulator, as opposed to the more conventional approach using electrostatic beams. Vibrational excitation cross sections are presented for CO, CO<sub>2</sub>, and H<sub>2</sub>. The 0.08 eV  $\nu_2$  bending mode is resolved in CO<sub>2</sub>, and measurements are presented for H<sub>2</sub> down to the threshold for vibrational excitation.

While some theoretical calculations have been made for vibrational excitation of molecules by positron impact [3,13–19], the list of molecules studied remains short, probably due in part to the lack of experimental data available for comparison. Experimental absolute cross sections can provide a strict test of these theoretical calculations. The experiments presented here represent the opening of a previously unexplored region of positron-matter interactions which will hopefully stimulate further experimental and theoretical work. The vibrational ex-

citation processes studied here also play a crucial role in the buffer-gas trapping and cooling techniques which are likely to be the basis of a new generation of positron sources [7,20].

The experiments are carried out using the technique previously developed to create a cold positron beam [12]. The beam is formed from a <sup>22</sup>Na positron source with a neon moderator and a buffer-gas positron accumulator [6,20]. Positrons are confined in a Penning-Malmberg trap with a 0.15 T magnetic field and cool to room temperature ( $\sim 25$  meV) by collisions on molecular nitrogen. Recently it was found that addition of a small amount of a suitably chosen molecular gas to the trap reduced the cooling time significantly [21,22]. For the experiments reported here, addition of  $\sim 5 \times 10^{-7}$  torr of SF<sub>6</sub> or CF<sub>4</sub> to the third stage of the accumulator reduced the cooling time by greater than a factor of 10 from when only N<sub>2</sub> was present (i.e., at a pressure  $\sim 2 \times 10^{-6}$  torr), thereby significantly increasing the data rate. As illustrated in Fig. 1, positrons from the accumulator are extracted as a beam by slowly raising the confining potential. The energy resolution of the beam can be as low as 18 meV (FWHM) [12], and the typical energy resolution of the beam used in these experiments was 25–30 meV. The energy spread of the beam is determined in part by space charge effects in the

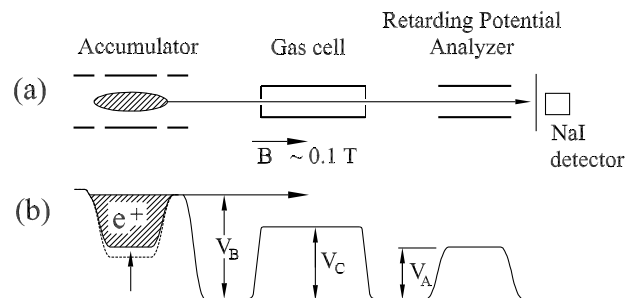


FIG. 1. (a) Schematic diagram of the experimental apparatus for the scattering experiments; (b) the potential profile for the electrodes: the potential  $V_B$  sets the beam energy exiting the accumulator,  $V_C$  is the potential of the gas cell, and  $V_A$  the potential of the RPA.

accumulator. As a result, in order to maintain a cold beam, beam pulses from the accumulator (duration  $\sim 2 \mu\text{s}$ ) were restricted to  $\leq 1 \times 10^5$  positrons for the measurements described here.

Referring to Fig. 1, the positrons are guided through the gas cell by a magnetic field of 0.095 T and through a retarding potential analyzer (RPA) by a field of up to 0.1 T (discussed in more detail below). The gas cell is a 38.1 cm long gold-plated copper cylinder, with an internal diameter of 7 cm and entrance and exit apertures of 0.5 cm. The pressure in the cell is measured using a capacitance manometer accurate to  $\pm 0.1\%$ . Differential pumping ensures that scattering events are restricted to the gas cell. Positrons passing through the RPA annihilate on a plate biased at  $-15\text{V}$ , and the  $\gamma$  rays from the annihilation events are detected using a NaI scintillation detector. This signal is directly proportional to the total number of positrons which are transmitted through the RPA.

The total energy  $E_T$  of a positron in a magnetic field of strength  $B$  can be divided into two components,  $E_T = E_\perp + E_\parallel$ , where  $E_\perp$  is the energy due to the cyclotron motion, and  $E_\parallel$  is the translational energy of the positron along the field. As discussed below, the analysis technique used to measure vibrational cross sections relies on the fact that the quantity  $E_\perp/B$  is an adiabatic invariant. The energy of the positron beam through the gas cell is  $E_T = e(V_B - V_C)$ , where  $V_B$  and  $V_C$  are the potentials of the accumulator and gas cell electrodes respectively, as shown in Fig. 1. Therefore, a typical positron in the beam will have  $E_\perp \sim 25 \text{ meV}$  and  $E_T \approx E_\parallel \gg E_\perp$ .

In the experiments reported here (i.e., beam energies below electronic excitation and positronium formation thresholds), elastic, vibrational, and rotational scattering events can occur. Positron energy loss due to rotational excitation is too small to be resolved in these experiments. For elastic scattering, the incident positron is scattered through some angle  $\theta$  but loses no total energy. In this case the angular scattering transfers energy from  $E_\parallel$  to  $E_\perp$ , so that  $E_\parallel = E_T \cos^2\theta$  and  $E_\perp = E_T \sin^2\theta$ . For vibrational excitation, the positron loses some of its total energy by exciting one of the vibrational modes of the molecule, and is also scattered at some angle. The positron beam is magnetically guided from the gas cell to the RPA, which transmits only positrons with  $E_\parallel > eV_A$ . Only the translational energy spread of the scattered beam is measured. Thus, when both vibrational and elastic scattering are present, it is impossible to distinguish between the two processes, since the spreads in  $E_\parallel$  from angular scattering due to these two processes can overlap.

This difficulty is illustrated in Fig. 2(a), which shows RPA data for CO at an incident positron energy of 0.5 eV. The spread due to the angular distribution of the scattering completely dominates the data, and it is not possible to distinguish vibrational from elastic scattering. However, by taking advantage of the adiabatic invariant  $E_\perp/B$ , the

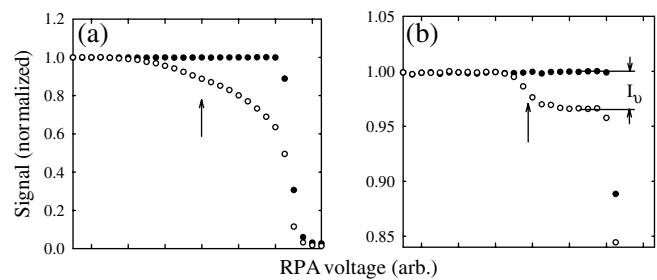


FIG. 2. (a) RPA measurement for CO with magnetic field ratio  $M = 1$ . The beam energy inside the gas cell is 0.50 eV, and the total scattering in this case is approximately 35% of the positron beam through the cell. (b) RPA measurement for CO with  $M = 35$ . As indicated by the arrow, the step due to the  $\nu_1$  vibrational excitation at 0.27 eV is clearly visible (spacing between the ticks on the x axis is 0.1 V). Note that the step size  $I_v$  is an order of magnitude smaller than the total scattering in (a), demonstrating the effectiveness of this technique in separating inelastic from elastic scattering.

effects of elastic scattering can be compressed into a narrow region near the beam cutoff. In this case, elastic and vibrational scattering can be separated. In particular, if the gas cell is located in a high field region, and the RPA is located in a low field region,  $E_\perp$  is reduced by the factor  $1/M$ , where  $M$  is the ratio of the magnetic field strengths. Since  $E_T$  is also conserved, energy is transferred from  $E_\perp$  into  $E_\parallel$ , resulting in a reduction of the spread in  $E_\parallel$  due to elastic scattering. For elastic scattering the maximum energy that can be transferred from  $E_\parallel$  into  $E_\perp$  is the total beam energy, which occurs at a scattering angle of  $90^\circ$ . Thus, when the RPA is located in a region of lower field, the resulting energy spread in  $E_\parallel$  due to the elastic scattering is reduced to  $E_T/M$ . Figure 2(b) shows the RPA data for CO with  $M = 35$  (i.e., 950 to 27 G). In this case the elastic scattering is confined to a small region within 15 mV of the beam cutoff, and the step produced by the vibrational excitation of the  $\nu_1$  mode of CO at 0.27 eV can clearly be resolved, even though the elastic scattering cross section is an order of magnitude larger. All inelastic scattering events are accounted for in the step.

The magnitude of the step  $I_v$  in Fig. 2(b), relative to the incident positron beam intensity  $I_0$  is used to determine the cross section through the relationship

$$\sigma_v(E) = \frac{28.6}{P} \frac{I_v}{I_0},$$

where  $P$  is the pressure (in mtorr) of the target molecule in the gas cell, and  $\sigma_v(E)$  is in units of  $a_0^2$ . The curve in Fig. 2 is closely approximated by the sum of two error functions, and the values of  $I_v$  and  $I_0$  are then determined by a least-squares fit of this function to the data. To verify that the cross sections obtained are independent of the pressure in the gas cell (e.g., that the effects of multiple scattering are negligible), measurements were made at several different gas pressures for each molecule.

Typical target gas pressures ranged from 0.2 to 1 mtorr depending on the total and vibrational cross sections.

Care has been taken to eliminate systematic errors. For example, each data set has been normalized independently, thus avoiding problems associated with detector calibration and long term drifts in the experiment. The error in the cross sections was then determined by the one sigma error in the fit to the RPA data. This is much larger than other potential sources of error, such as errors in the scattering length or pressure measurements. Systematic effects were observed at energies below 0.5 eV, possibly due to scattering at angles greater than  $90^\circ$ . For this reason, no measurements are reported below this energy. Work is underway to address these problems, to allow the investigation of the threshold behavior of vibrational excitation, which is potentially an interesting aspect of positron-molecule interactions.

The energy of the vibrational transitions can be determined to about  $\pm 3\%$  by the data. More precise values and identification of the specific modes quoted here are taken from optical and electron scattering experiments [23]. The test molecules were studied at room temperature, so all transitions are assumed to be  $\nu = 0 \rightarrow 1$ , averaged over initial rotational states.

Data are shown in Fig. 3 for the  $\nu_1$  mode of CO at 0.27 eV. The experimental results are compared with the calculations of Gianturco *et al.* [15] and Jain [16]. There is excellent agreement with the calculation by Gianturco *et al.*, while the calculations of Jain are lower by a factor of approximately 2 but describe quite well the qualitative behavior of the cross section. Gianturco *et al.* speculate that the sharp onset from threshold may be due to the presence of an  $e^+ - \text{CO}$  resonance. This is worthy of further study since, to our knowledge, it would be the first direct evidence of such a resonance.

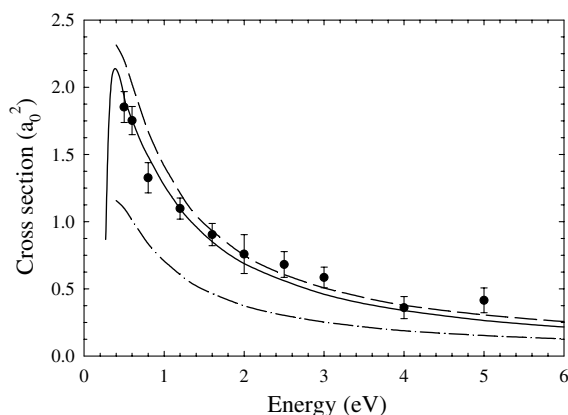


FIG. 3. Cross section for excitation of the  $\nu_1$  vibrational mode of CO. Circles are the experimental data, the solid line is the theory of Gianturco *et al.* [15], the dot-dash line is the theory of Jain [16], and the dashed line is Jain's theory multiplied by a factor of 2. Note there are no fitted parameters between experiment and the theories.

Figure 4 shows the cross sections for excitation of the  $\nu_2$  (bending) and  $\nu_3$  (asymmetric stretch) modes of  $\text{CO}_2$  at 0.08 and 0.29 eV, respectively. The measurements of the two cross sections were able to be made simultaneously, demonstrating the versatility of the experimental approach. To illustrate this, the raw data for these measurements are shown in the inset of Fig. 4. The data are compared to the calculations of Kimura *et al.* [13]. The agreement is excellent for the  $\nu_3$  mode at energies where a comparison is possible. For the  $\nu_2$  mode, the measurements are just below the energy of the lowest available calculation. However, it appears that the predictions for this mode are somewhat lower than the extrapolation of the experimental data. The energy range for the  $\nu_2$  measurement was limited due to elastic scattering. If a larger ratio  $M$  were available, this energy range could be extended, and work is currently underway to achieve this. Calculations predict that the cross section for the  $\nu_1$  (symmetric stretch) mode is 2 orders of magnitude lower than for the other modes [13,14], consistent with the fact that it was not observed.

Hydrogen differs from the previous two molecules studied, in that it is a homonuclear diatomic molecule. The vibrational excitation has no dipole component, and so it is not easily excited by positron impact. Experimental data for the  $\nu_1$  mode in  $\text{H}_2$ , which has an energy of 0.55 eV, are presented in Fig. 5. The cross section for this excitation is much lower than those for CO and  $\text{CO}_2$ , which is likely due to the lack of dipole coupling to the mode in  $\text{H}_2$ . The experimental data are in good agreement with the calculations of Sur and Ghosh [18]. The predictions of Baille and Darewych [19] are lower, although at energies above 2 eV they are closer to the experimental measurements. A calculation for this cross section published by Gianturco and Mukherjee [17] is lower by 2 orders of magnitude. Recent communication with these authors has uncovered an

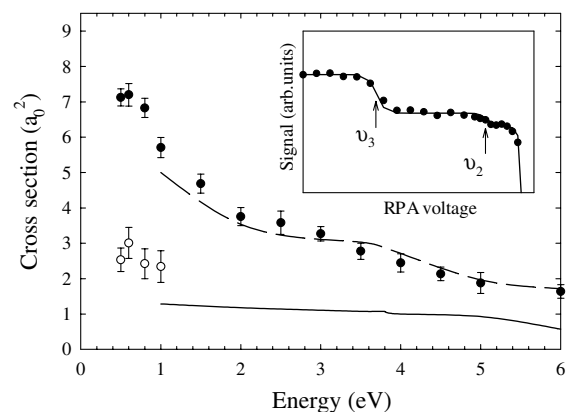


FIG. 4. Cross section for excitation of the  $\nu_2$  and  $\nu_3$  vibrational modes of  $\text{CO}_2$ . Open circles and closed circles are experimental data for the  $\nu_2$  and  $\nu_3$  modes, respectively. Solid line and dashed line are the theory of Kimura *et al.* [13] for the same two modes. There are no fitted parameters. Inset: RPA data, showing steps due to both vibrational modes. The solid line is the fitted curve (see text for further details).

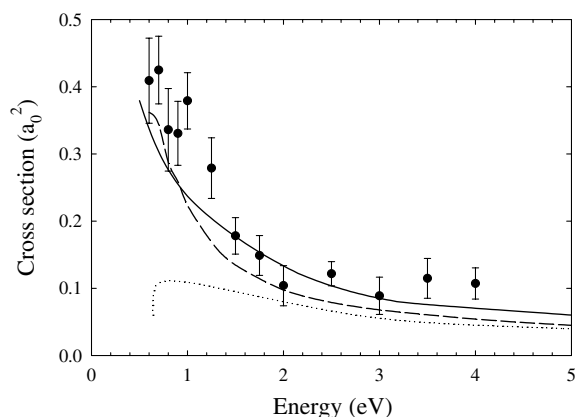


FIG. 5. Cross section for excitation of the  $v_1$  vibrational mode of  $H_2$ . Circles are the experimental data. Solid line is the theory of Sur and Ghosh [18], and dotted line is the theory of Baille and Darewych [19]. The dashed line is the corrected results of Gianturco and Mukherjee [24] (see text). There are no fitted parameters between experiment and theory.

error in the polarization parameters used for the calculation, and their corrected results are shown as the dashed line in Fig. 5 [24].

The work described here marks the opening of a new area for experimental investigation of positron-molecule collisions. Cross sections have been measured for the vibrational excitation of CO, CO<sub>2</sub>, and H<sub>2</sub> by positron impact. In the case of CO<sub>2</sub>, two different modes were able to be studied. Good agreement between the experiments and theory is found for CO and CO<sub>2</sub>. Two of the calculations for H<sub>2</sub> are in good agreement with the experimental data.

Theoretical calculations for vibrational excitation by positron impact are currently available for only a few other molecules, and there are no other experimental data available for this process beyond that presented here and in Ref. [4]. With the capabilities of the positron beam and the adiabatic measurement technique described here, we anticipate that an extensive program of measurements can now be undertaken. Further theoretical work in this area would be most valuable. We are currently developing techniques to create a cryogenic plasma (e.g.,  $T \sim 10$  K) which, in principle, will allow the formation of colder positron beams and the investigation of positron scattering at much lower energies.

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- [1] W.E. Kauppila and T.S. Stein, *Adv. At. Mol. Opt. Phys.* **26**, 1 (1990).
  - [2] M. Kimura, O. Sueoka, A. Hamada, and Y. Itikawa, *Adv. Chem. Phys.* **111**, 537 (2000).
  - [3] F.A. Gianturco and T. Mukherjee, *E. Phys. J. D* **7**, 211 (1999).
  - [4] S.J. Gilbert, R.G. Greaves, and C.M. Surko, *Phys. Rev. Lett.* **82**, 5032 (1999).
  - [5] G. Laricchia and M. Charlton, *Philos. Trans. R. Soc. London A* **357**, 2259 (1999).
  - [6] R.G. Greaves and C.M. Surko, *Phys. Plasmas* **4**, 1528 (1997).
  - [7] R.G. Greaves and C.M. Surko, in *Nonneutral Plasma Physics III*, edited by J. Bollinger *et al.*, AIP Conf. Proc. No. 498 (AIP, New York, 1999), pp. 19–28.
  - [8] P.J. Schultz and K.G. Lynn, *Rev. Mod. Phys.* **60**, 701 (1988).
  - [9] O. Sueoka and A. Hamada, *J. Phys. Soc. Jpn.* **62**, 2669 (1993).
  - [10] O. Sueoka and S. Mori, *J. Phys. B* **19**, 4035 (1986).
  - [11] K.R. Hoffman *et al.*, *Phys. Rev. A* **25**, 1393 (1982).
  - [12] S.J. Gilbert, C. Kurz, R.G. Greaves, and C.M. Surko, *Appl. Phys. Lett.* **70**, 1944 (1997).
  - [13] M. Kimura *et al.*, *Phys. Rev. Lett.* **80**, 3936 (1998).
  - [14] F.A. Gianturco and T. Mukherjee, *J. Phys. B* **30**, 3567 (1997).
  - [15] F.A. Gianturco, T. Mukherjee, and P. Paoletti, *Phys. Rev. A* **56**, 3638 (1997).
  - [16] A. Jain, *J. Phys. B* **19**, L379 (1986).
  - [17] F.A. Gianturco and T. Mukherjee, *Phys. Rev. A* **55**, 1044 (1997).
  - [18] S. Sur and A.S. Ghosh, *J. Phys. B* **18**, L715 (1985).
  - [19] P. Baille and J.W. Darewych, *J. Phys. Lett.* **35**, 243 (1974).
  - [20] C.M. Surko, S.J. Gilbert, and R.G. Greaves, in *Non-Neutral Plasma Physics III*, edited by J. Bollinger *et al.* (American Institute of Physics, New York, 1999), pp. 3–12.
  - [21] R.G. Greaves and C.M. Surko, *Phys. Rev. Lett.* **85**, 1883 (2000).
  - [22] There is also an extensive literature concerning positron cooling at high neutral gas pressures. See, for example, I. Al-Qaradawi, M. Charlton, I. Borozan, and R. Whitehead, *J. Phys. B* **33**, 2725 (2000), and references therein.
  - [23] S.V. Khristenko, A.I. Maslov, and V.P. Shevelko, *Molecules and Their Spectroscopic Properties* (Springer-Verlag, Berlin, 1998).
  - [24] F.A. Gianturco (private communication).