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Resonant positron annihilation in ammonia

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Abstract. Positron annihilation in ammonia is analyzed using the framework of resonant annihilation [G. F. Gribakin and C. M. R. Lee, Phys. Rev. Lett. **97**, 193201 (2006)]. In particular, we show that molecular rotations can have a measurable effect on the annihilation rates at room temperatures. Rotation leads to broadening of vibrational Feshbach resonances. Rotations also allow a distinct contribution at low positron energies in the form of a rotational Feshbach resonance. This resonance can enhance the annihilation rate for thermalized room-temperature positrons. Comparison of theory and experiment shows that overtone and combination vibrations, including those due to inversion doubling, likely play an important role.

1. Introduction

The purpose of this work is to analyze the role of resonances in the positron annihilation in ammonia (NH_3). In particular, we estimate the effect of molecular rotations in broadening the observed vibrational resonances. A new type of resonance which can occur at very low positron energies for molecules with nonzero permanent dipole moments is also identified. This *rotational Feshbach resonance* can have a sizeable affect on the annihilation of thermal positrons in small polar molecules.

Resonant processes have long been suspected to be the origin of anomalously large positron annihilation rates observed in many polyatomic gases [1, 2, 3, 4]. This explanation remained a hypothesis until vibrational resonances were actually observed using a high-resolution trap-based positron beam [5]. Since then, this technique has been used to measure the annihilation rates as a function of the positron energy for a large number of large and small polyatomic molecules [6, 7, 8, 9].

In general, vibrational Feshbach resonances (VFR) can be observed in molecules capable of binding the positron. They occur when an incident positron with energy $\varepsilon > 0$ is captured into the bound state at negative energy $-\varepsilon_b$, the energy $\varepsilon + \varepsilon_b$ being transferred into the vibrational motion of the positron-molecule complex. The energy conservation for this process determines the energies of the resonances,

$$\varepsilon_\nu = E_\nu - \varepsilon_b, \tag{1}$$

where ε_b is the positron-molecule binding energy, and E_ν is the energy of the molecular vibrational excitation. According to Eq. (1), the VFRs are downshifted relative to the vibrational excitation energies by the positron binding energy. Observation of resonances thus allows one to measure ε_b. At present, positron binding energies for about 30 molecules have been determined in this way [10].

Theoretically, resonant annihilation can be described using the simple Breit-Wigner formalism [3, 4]. Its application, however, requires knowledge of the positron-molecule binding energy, vibrational excitation energies of the positron-molecule complex (including combination vibrations and overtones), as well as the total and partial widths of the resonances, i.e., those for annihilation and positron detachment. So far, it has been possible to calculate the annihilation rates only for small-sized polyatomic molecules with infrared-active modes, such as protonated and deuterated methyl halides [11, 12]. The binding energy is a free parameter in the theory. It is determined by comparison with the energy-resolved experimental annihilation rates. Besides methyl halides, the theory also provided a good description of the experiment in ethanol [9] and methanol, in which a contribution from overtones and combination vibrations had to be included [12]. Its application to small polyatomics in which not all modes are infrared active, e.g., acetylene and ethylene, indicates that VFR of infrared-inactive modes, as well as overtones and combinations, need to be considered to explain the experimental data.

Ammonia is the smallest molecule with infrared-active modes whose annihilation rate has been measured [9, 13]. It does not show the vibrational resonances as clearly as the molecules mentioned above. However, the magnitude of the annihilation rate suggests that it contains a large contribution of resonant annihilation. In this paper we use the theory of Ref. [11] and its extension in order to understand the details of positron annihilation in NH_3.

2. Resonant annihilation

The positron annihilation cross section for many-electron targets is usually parameterized in terms of the effective number of electrons Z_{eff},

$$\sigma_a = \pi r_0^2 \frac{c}{v} Z_{\text{eff}}, \tag{2}$$

where r_0 is the classical electron radius, c is the speed of light, and v is the positron velocity. The *resonant* contribution to the annihilation cross section can be estimated using the Breit-Wigner theory [3, 4], which yields

$$Z_{\text{eff}}^{(\text{res})} = \frac{\pi}{k}\rho_{ep}\sum_{\nu}\frac{g_\nu \Gamma_\nu^e}{(\varepsilon-\varepsilon_\nu)^2+\Gamma_\nu^2/4}. \tag{3}$$

Here Γ_ν^e and Γ_ν are the elastic and total widths of νth resonance, g_ν is its degeneracy, k is the positron momentum and ρ_{ep} is the average electron density at the positron in the bound state (atomic units are used throughout). This density determines the annihilation width of the resonances,

$$\Gamma^a = \pi r_0^2 c \rho_{ep}. \tag{4}$$

It scales with the binding energy as $\rho_{ep} = F\kappa/2\pi$, where $\kappa = \sqrt{2\varepsilon_b}$, and $F \approx 0.66$ [4]. The same parameters determine the contribution of *direct* annihilation, $Z_{\text{eff}}^{(\text{dir})} \simeq F/(\kappa^2+k^2)$ [3].

To compare with experiment, the normalized annihilation rate, Z_{eff}, must be averaged over the positron beam energy distribution. For the resonant part, this can be done analytically [11],

$$\bar{Z}_{\text{eff}}^{(\text{res})}(\epsilon) = 2\pi^2\rho_{ep}\sum_{\nu}\frac{g_\nu\Gamma_\nu^e}{k_\nu\Gamma_\nu}\Delta(\epsilon-\varepsilon_\nu), \tag{5}$$

where $k_\nu = \sqrt{2\varepsilon_\nu}$, and the function $\Delta(E)$ describes the shape of a narrow resonance (e.g., $\Gamma_\nu \lesssim 1$ meV) observed with the trap-based positron beam (note that a factor 1/2 is missing in Eq. (10) of Ref. [11]),

$$\Delta(E) = \frac{1}{2k_BT_\perp}\exp\left[\frac{\sigma^2}{2(k_BT_\perp)^2}\right]\exp\left(\frac{E}{k_BT_\perp}\right)\left\{1+\Phi\left[-\frac{1}{\sqrt{2}}\left(\frac{E}{\sigma}+\frac{\sigma}{k_BT_\perp}\right)\right]\right\}. \tag{6}$$

Here $T_\perp$ is the transverse temperature of the positron beam, $\sigma = \delta_z/\sqrt{8\ln 2}$, δ_z being the full width at half maximum of the longitudinal energy distribution, k_B is Boltzmann's constant, and $\Phi(x)$ is the error function. The typical experimental values are $k_B T_\perp = \delta_z = 25$ meV.

The elastic resonance widths of infrared-active vibrational excitations can be estimated using their transition dipole amplitudes d_ν and frequencies ω_ν [11],

$$\Gamma_\nu^e = \frac{16\omega_\nu d_\nu^2}{27}\, h(\xi), \tag{7}$$

where $h(\xi) = \xi^{3/2}(1-\xi)^{-1/2}\left[{}_2F_1\left(\frac{1}{2},1;\frac{5}{2};-\xi/(1-\xi)\right)\right]^2$ is a dimensionless function of $\xi = 1 - \varepsilon_b/\omega_\nu$. Owing to the weakness of positron binding ($\varepsilon_b \sim$ 1–10 meV for small polyatomics), one can also assume that the vibrational excitation energies of the positron-molecule complex are close to those of the neutral molecule, $E_\nu \approx \omega_\nu$. The values of ω_ν of d_ν for many molecules are known from infrared absorption measurements [14].

The elastic width of a typical infrared-active VFR, $\Gamma_\nu^e \lesssim 0.1$ meV, is much larger than its annihilation width, e.g., $\Gamma^a = 0.1$ μeV for $\varepsilon_b = 10$ meV. The total width Γ_ν is then dominated by the elastic width (unless positron detachment accompanied by vibrational excitation of the molecule, i.e., vibrationally inelastic escape, is important). In this case the ratio Γ_ν^e/Γ_ν in Eq. (5) is close to unity, and the contribution of each resonance for a given molecule is determined by the factor g_ν/k_ν. In fact, one can also use Eq. (5) with $\Gamma_\nu^e/\Gamma_\nu = 1$ to estimate the contribution of VFR involving infrared-inactive modes. For these modes the long-range dipole interaction which results in Eq. (7), is zero, so the positron coupling to these modes is probably weaker. However, because of the smallness of Γ^a, they may still satisfy $\Gamma_\nu^e > \Gamma^a$, making $\Gamma_\nu^e/\Gamma_\nu \approx 1$ a reasonable assumption.

The NH_3 molecule has four vibrational modes with frequencies $\omega_\nu = 414$, 118, 427 and 201 meV, dipole amplitudes $d_\nu = 0.0095$, 0.0981, 0.0054 and 0.0227 a.u., and degeneracies $g_\nu = 1$, 1, 2 and 2, for the modes 1 to 4, respectively [14]. Using these values and assuming a small binding energy of $\varepsilon_b = 2$ meV, we obtain $\bar{Z}_{\text{eff}}^{(\text{res})}$ from Eq. (5). It is shown in Fig. 1 together with the positron-energy averaged $Z_{\text{eff}}^{(\text{dir})}$. One can immediately see that the theoretical resonances are much sharper than any features of the experimental Z_{eff} spectrum. The choice of the binding energy used is rather arbitrary. Apart from a small energy shift described by Eq. (1), the binding energy affects the overall magnitude of $Z_{\text{eff}}^{(\text{res})}$ through the factor $\rho_{ep} \propto \sqrt{\varepsilon_b}$. Hence, the value chosen is a compromise between describing the features of the experimental data at low (0.1–0.2 eV) and high (0.35–0.45 eV) energies. Theory also fails to account for the signal between the resonance groups. This situation is in stark contrast to that in methyl halides, where theory and experiment are in good agreement [11, 12]. In the following sections we analyze effects which may account for this discrepancy.

3. Rotational broadening of VFR

In all previous estimates of resonant annihilation, rotations have been neglected. The positron-molecule bound states is likely to be the fully symmetric, i.e., A_1 or A_g. For smaller molecules and weak binding it is largely of s-wave character, behaving like a bound state in a zero-range potential $\varphi(\mathbf{r}) \simeq Ar^{-1}e^{-\kappa r}$ at large positron-molecule separations r. The incident positron wave function at low energies is also dominated by the s-wave component. In this case the positron capture into a VFR does not change the total angular momentum J of the molecule. This situation is realized in the zero-range potential model of positron annihilation with a dimer [15, 16].

For VFRs of infrared-active vibrations, the positron is captured into the symmetric bound state from the incident p wave. The selection rule for the vibrational and rotational transition is the same as for infrared absorption. For a symmetric top molecule, such as ammonia, this means

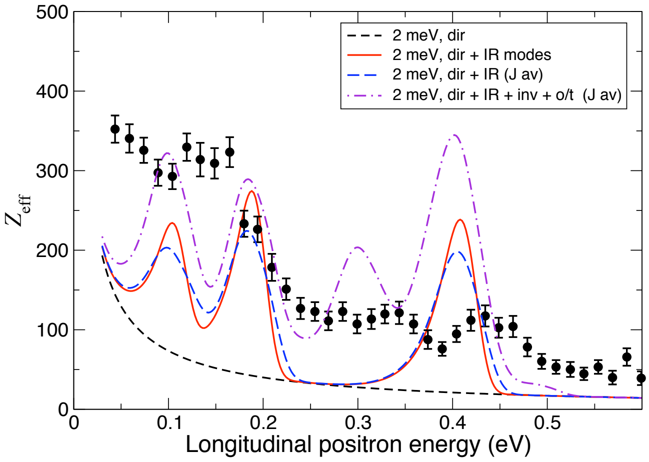

Figure 1. Normalized positron annihilation rate $Z_{\rm eff}$ in ammonia. Experimental data (●) obtained with the trap-based positron beam [13] (see also [9]). Theory (for $\varepsilon_b = 2$ meV): − − −, $Z_{\rm eff}^{\rm (dir)}$; ——, total $Z_{\rm eff} = Z_{\rm eff}^{\rm (dir)} + Z_{\rm eff}^{\rm (res)}$, including only mode-based VFR; — — —, total $Z_{\rm eff}$ with the resonances broadened by rotations at 300 K; — · —, total $Z_{\rm eff}$ including VFR due to the modes, inversion doubling and combination vibrations (rotationally broadened) .

$\Delta J = 0, \pm 1$, and $\Delta K = 0$ or $\Delta K = \pm 1$, depending on whether the transition moment is parallel or perpendicular to the molecular axis [17]. Here K is the quantum number of the component of the angular momentum along the molecular axis. Together, the J and K determine the rotational energy,

$$E_{JK} = BJ(J+1) + (C-B)K^2, \tag{8}$$

where $B = 1/2I_B$ and $C = 1/2I_C$, I_B and I_C being the principal moments of inertia perpendicular and parallel to the molecular axis. For ammonia the rotational constants are $B = 1.23$ meV and $C = 0.77$ meV [18].

In a dipole transition the rotational quantum numbers and the rotational energies of the initial and final state are different. This means that in an ensemble of molecules with different J and K, a number of resonances will appear near the energy ε_ν. Their statistical weights will depend on the Boltzmann factors $\exp(-E_{JK}/k_BT)$, where T is the molecular temperature. In current room-temperature experiments the energy spread of the positron beam is larger than the rotational energy shifts ΔE_{JK}. Hence, the energy shifts will lead to additional broadening of the observed resonances.

For a simple of estimate of this effect, we replace the symmetric top with a spherical top, characterized by the single average rotational constant $\bar{B}$, $3/\bar{B} = 2/B + 1/C$, i.e., $\bar{B} = 1.02$ meV for NH$_3$. Its rotational energy levels,

$$E_J = \bar{B}J(J+1) \tag{9}$$

are $(2J+1)^2$ degenerate, with populations $w_J = Z^{-1}(2J+1)^2 \exp(-E_J/k_BT)$, where

$$Z = \sum_J (2J+1)^2 \exp(-E_J/k_BT). \tag{10}$$

For $\Delta J = \pm 1$ transition, the rotational energy shifts are $\Delta E_{J+1,J} = 2\bar{B}(J+1)$. Adding these shifts to the resonance energies ε_ν, we average $Z_{\rm eff}^{\rm (res)}$ due to mode-based VFR over J with probabilities w_J. The result is shown by the long-dashed curve in Fig. 1. For the most probable J value, $J \sim \sqrt{2k_BT/\bar{B}} \sim 7$ at $T = 300$ K, the rotational broadening is $\Delta E_{J+1,J} \sim 2\sqrt{2k_BT\bar{B}} \sim 15$ meV. This broadening of the VFRs is indeed noticeable in Fig. 1. However, the calculated resonances remain sharper than the measured Z_{eff}.

4. Rotational Feshbach resonance in NH$_3$

Another possible effect in ammonia is due to its the permanent electric dipole moment, $\mu = 1.47$ debye $= 0.578$ a.u. [19]. The positron interaction with the dipole, $V = \boldsymbol{\mu}\cdot\mathbf{r}/r^3$, can lead to positron capture accompanied by a *rotational* $J \to J+1$ excitation of the molecule. This resonance capture will occur at the positron energy

$$\varepsilon_J \equiv k_J^2/2 = 2\bar{B}(J+1) - \varepsilon_b. \tag{11}$$

The elastic width of the corresponding rotational Feshbach resonance (RFR) can be estimated similarly to that of the VFR of infrared-active modes [11],

$$\Gamma_J^e = \frac{8k_J^3}{27\kappa}\,\frac{J+1}{2J+1}\left|{}_2F_1\left(\tfrac{1}{2},1;\tfrac{5}{2};-\varepsilon_J/\varepsilon_b\right)\right|^2, \tag{12}$$

cf. Eq. (7). An estimate of this width shows that $\Gamma_J^e \gg \Gamma^a$, which means that the RFR will contribute to positron annihilation in the same way as any VFR. Note that RFRs were considered earlier in the context of low-energy electron collisions with simple molecules [20].

For NH$_3$ at room temperature with $J \sim 7$, the RFR will occur in the range of positron energies $\varepsilon \sim 15$ meV. This energy is much lower than what can currently be measured with the positron beam. However, a resonance at such low energy will certainly affect Z_{eff} values for *thermalized* positrons. Indeed, using the same value $\varepsilon_b = 2$ meV, we obtain room-temperature Maxwellian averages of $Z_{\mathrm{eff}}^{(\mathrm{dir})} = 450$ and $Z_{\mathrm{eff}}^{(\mathrm{res})} = 480$. Here about 98% of $Z_{\mathrm{eff}}^{(\mathrm{res})}$ is due to the RFR. This contribution significantly reduces the gap between the theoretical $Z_{\mathrm{eff}} = Z_{\mathrm{eff}}^{(\mathrm{dir})} + Z_{\mathrm{eff}}^{(\mathrm{res})} = 930$, and the experimental room-temperature value, $Z_{\mathrm{eff}} = 1300$ [21].

5. Inversion doubling, overtones and combinations

As seen from the estimates in Secs. 3 and 4, molecular rotations cannot account for the discrepancy between the theory for mode-based VFRs and experiment. It appears that there must be some additional resonances which boost the annihilation rate below 0.15 eV and around 0.3 eV.

The spectrum of low-lying vibrational levels of ammonia is well known, both experimentally and theoretically (see, e.g., Refs. [22, 23]). In particular, NH$_3$ is a classic example of a molecule with inversion doubling. This occurs as a result of tunneling of the nitrogen atom through the plane of the hydrogen atoms. Thus, each vibrational level is split into two sublevels, a lower positive (+) and an upper negative parity level (−) [17]. The selection rule for infrared absorption, $+ \leftrightarrow -$, means that in spite of the doubling of the modes, only four fundamental transitions will be allowed from either component of the vibrational ground state (split by 0.79 cm^{-1}). However, if positron capture is accompanied by $+ \leftrightarrow +$ or $- \leftrightarrow -$ transitions, the number of mode-based resonances accessible from either component of the ground state doubles.

In addition, the energy range of interest (0–4100 cm^{-1}) contains a few overtones and combination vibrations. To assess the effect of their VFRs on the annihilation rate, we assume that these resonances have elastic widths $\Gamma_\nu^e \gg \Gamma^a$. We also moderate the contribution of overtones and combinations (somewhat arbitrarily) by the factor $\Gamma_\nu^e/\Gamma_\nu = 1/n$, where n is the total number of vibrational quanta in the excitation. A possible reason for such weighting is that a multiquantum vibrational excitation allows the positron to escape through a number of (vibrationally inelastic) detachment channels. Using the data from Table 2 of Ref. [23] and

Table 3 of Ref. [22], a total of 17 vibrational excitations are included, namely: ν_2 (+ and −), $2\nu_2$ (+ and −), $3\nu_2$ (+ and −), $4\nu_2$ (+ and −), ν_4, $\nu_2+\nu_4$ (+ and −), $2\nu_4$ (A_1), $2\nu_4$ (E), ν_1, ν_3, and $2\nu_2+\nu_4$ (+ and −).

The result of this calculation (which also included rotational broadening, as described in Sec. 3) is shown in Fig. 1 by the dot-dashed curve. The additional VFRs have built up spectral weight around 0.1 eV, and around 0.3 eV, i.e., in the gap between the modes. The calculation appears to be in better overall agreement with experiment, except for the strong overestimation of the peak at 0.4 eV. This suggests that the vibrational excitations listed above do indeed play a role in VFR and contribute to the positron annihilation. It is also clear that in ammonia one needs to calculate, rather then estimate, the elastic and total widths. This must be done for both infrared-allowed and infrared-forbidden (but "positron-allowed") transitions, including the inelastic escape channels for overtones and combinations.

6. Conclusions

Positron annihilation in ammonia has been analyzed using the resonant annihilation theory. Comparison with experiment indicates that vibrational resonances due to inversion doubling, as well as overtones and combination vibrations, all contribute to the annihilation rate for positron energies below 0.5 eV.

Due to the large rotational constants, the vibrational resonances in ammonia are significantly broadened by molecular rotations at room temperature. The permanent dipole moment (or, equivalently, the ground-state inversion doublet) gives rise to a rotational Feshbach resonance at sub-thermal positron energies. This resonance plays an important role in enhancing annihilation for room-temperature positrons.

It is possible that rotational Feshbach resonances can also occur in other small polyatomic molecules with small positron binding energies. In nonpolar molecules, the low-energy positron can couple to molecular rotations by means of the electrostatic quadrupole interaction.

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